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Benzene Continuous Emission Monitoring Systems for Gasoline Bulk Storage

Pacific Environmental Services, Inc., Reston, VA

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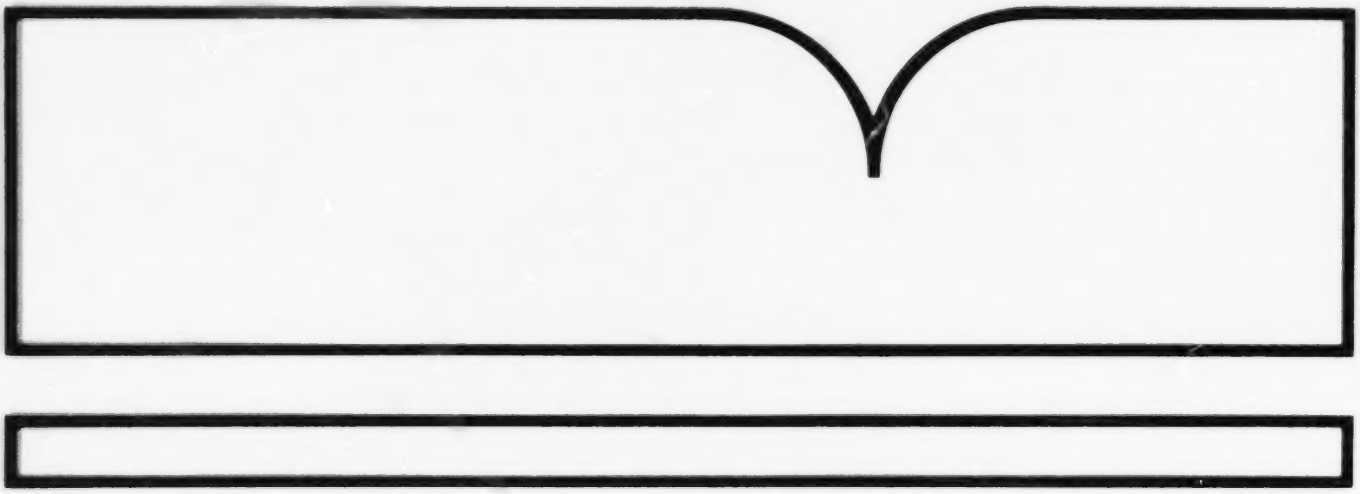

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BENZENE CONTINUOUS EMISSION MONITORING SYSTEMS FOR GASOLINE BULK STORAGE

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PROJECT REPORT
Contract No. 68-02-3887
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16. ABSTRACT

This report summarizes a study of continuous emission monitors for measuring benzene emissions from gasoline bulk storage terminals. The work was performed for the Quality Assurance Division, Source Branch, of the U.S. Environmental Protection Agency by Pacific Environmental Services under Contract No. 68-02-3997, Task 33. The Environmental Protection Agency is considering regulating the emissions of benzene from bulk storage of gasoline products and is likely to require data regarding benzene emissions. The evaluation of continuous emission monitors for benzene is a necessary part of the overall effort.

This study was performed in three phases: a literature review, a laboratory evaluation, and a field evaluation. The study objectives were to determine the commercial availability of continuous monitors for benzene and the reported performance of these units, evaluate their suitability for measuring benzene in gasoline vapors, and determine their applicability to the source category.

There are no benzene-specific continuous emission analyzers commercially available. If a benzene-specific system is required, and semicontinuous (i.e. gas chromatographic analysis) is not acceptable for regulatory purposes, nondispersive ultraviolet analysis holds promise for accomplishing this task. The nondispersive ultraviolet technique can be used to measure benzene in a matrix of other hydrocarbons, and nondispersive ultraviolet continuous systems do exist, so combining the laboratory experience with the continuous monitor experience into a prototype benzene continuous monitor appears to be a promising (and cost-effective) means to obtain such an instrument.

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SECTION 1

INTRODUCTION

BACKGROUND

The U.S Environmental Protection Agency (EPA) is considering regulating benzene emissions from the gasoline bulk storage industry. A means of continuously measuring benzene emissions may be required if the regulation contains specific emission limits and if it contains a CEM requirement. If the regulation contains specific hardware requirements or operating practices, measurement of a process parameter or benzene surrogate might be appropriate. This study was undertaken to evaluate the current availability and performance of continuous emission monitors (CEMs) for benzene in the event that continuous benzene monitoring was deemed necessary in the regulation. This investigation focussed on the availability and performance of existing commercial instruments, but the findings are intended to serve as the basis for development of a test method suitable for Federal Register promulgation.

PURPOSES

Three distinct objectives were identified as pertinent to this study. The first objective was to evaluate the availability of commercial monitors to measure benzene at gasoline bulk terminals to determine the extent and nature of any further study. The second objective was to characterize the performance characteristics of any available units to determine, in a general way, their applicability to the source category and measurement requirements of the Agency. Third, after the performance characteristics of the available units were evaluated, the study was to define any additional requirements or modifications to existing instruments likely to be needed for purposes of setting National Emission Standards for Hazardous Air Pollutants (NESHAPs).

SCOPE

The only source category being considered in this study is the gasoline bulk storage industry, although the results may apply to other source categories (e.g., maleic anhydride, styrene, phenol). Benzene is the only pollutant of interest for this study, although total hydrocarbon emission, as measured by the total hydrocarbon analyzers studied, was considered as a possible surrogate for benzene. A surrogate measure of benzene emissions was considered in case the Agency elected to pursue a regulatory approach using measurement of some process parameter or other

stack gas characteristic in lieu of direct benzene measurements. The scope of this study did not include quantification of the mass discharge rate of benzene; it did include evaluation of the technical feasibility of continuously monitoring benzene concentration in the exhaust gas and the capability of the analyzer(s) to distinguish benzene from other aliphatic and aromatic hydrocarbons and respond to changes in benzene concentrations in a timely manner. To a lesser extent, the scope included definition of what method development work might be required for an NESHAPs monitoring standard. Thus, the intent was not to develop an NESHAPs test method, but rather to ensure that the results of this study would be usable as preliminary method development studies, should the occasion arise.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Availability and Performance of Existing Instruments

Currently, no commercial analyzer is available that can continuously monitor benzene in the exhaust gas from a bulk gasoline storage terminal. There are process gas chromatographs (GCs) available that are designed for field use that could be modified to serve as semicontinuous analyzers and to perform the measurements with acceptable precision and accuracy. However, they are usually expensive and are generally used when their installation and operating costs are offset by improvements in product quality. If "continuous" analysis is to be performed, there are inexpensive combustibles, or total hydrocarbon analyzers, that could be modified to measure in the range of hydrocarbon concentrations expected, but the results would not relate to benzene emissions unless there were data to correlate total hydrocarbons with benzene.

Several different configurations of GCs could accomplish the requisite benzene separation and quantification. Either FIDs or PIDs could be used and isothermal operation of packed-columns would be acceptable. A heated column is not necessary to achieve the benzene separation from the other components of gasoline vapor, but might be necessary to achieve analytical cycle times short enough for the GC to be useful as a semicontinuous instrument.

Potential for Other Methods

Only one methodology seems to hold much promise for near-term development as a continuous benzene monitor, nondispersive ultraviolet (NDUV) analysis. Commercial NDUV instruments are used for other analytes, allowing many of the operating problems and issues to be resolved. The basic unknowns are whether a reasonable-cost unit could be built that combined the needed sensitivity and interference-rejection capabilities to measure ppm-level benzene in a gas stream containing percent-level hydrocarbons, including other aromatic compounds. Although other procedures still in their infancy, such as tunable atomic line molecular spectroscopy (TALMS), hold promise, sufficient data do not exist to assess the probable performance of such instruments.

Application to Gasoline Bulk Storage Terminals

Some of the requirements for a benzene CEM would depend on the regulation, and others would depend on source-related parameters. Examples of source-related parameters are the potential need for an explosion-proof instrument if placed on the stack, and variability in concentration and composition, depending on the type of control device (refrigeration, carbon absorber, or thermal oxidizer).

RECOMMENDATIONS

The NDUV technique for benzene monitoring holds sufficient promise to warrant further investigation. Some manufacturers have expressed an interest in pursuing this development. This could permit relatively inexpensive (to EPA) research. A prototype instrument could be built and subjected to laboratory and short-term field tests similar to those described in this report to establish the necessary performance specification data for the applicable regulations.

Should the Agency decide that a surrogate monitor is desirable, a substantial effort and much data would be required to relate the surrogate measure to benzene emissions. Assessing the effect of product liquids handled and of terminal and control device operating conditions on benzene emissions and on the surrogate parameter would require a major effort. Limited field tests indicate that such a correlation between total hydrocarbon and benzene emissions is highly unlikely. However, the limited testing performed suggests that the LEL-type analyzers do indicate the hydrocarbon emissions and could be used as an indicator of the operating condition of the control device.

The use of a dedicated GC also warrants investigation if one analysis every 3 to 5 min. is considered adequate. An application-specific unit would need to be tested to establish performance characteristics, because extrapolation of the data from this study would not reflect long-term unattended operation.

SECTION 3

EXPERIMENTAL DESIGN

GENERAL

A three-phase approach was taken corresponding to the three general purposes of the study. Phase I was a literature review of the analytical principles for determining benzene and a survey of the available commercial instrumentation. Phase II was laboratory testing of candidate instruments to verify precision and accuracy. Phase III was field testing the instruments. Each phase was concluded before the succeeding phase was begun, and the original plans were modified as dictated by the results of the preceding investigations.

LITERATURE REVIEW

The first step in the literature review phase was to investigate the reported analytical procedures for measuring benzene. The scope of the investigation was to include all potential procedures, not just those procedures currently used for continuous emission monitoring. It was expected that the number and type of commercial monitors would be limited and that some other methods might be adaptable or could form the basis for a new application. Concurrently, the technical literature was reviewed to establish the expected range of total hydrocarbon emissions and the benzene fraction of the total emissions from the bulk storage industry. As the second step, manufacturers of chemical analysis instrumentation were surveyed by both direct contact and through the literature to ascertain: the types of analyzers being produced; their suitability for use in an explosion-prone environment; their range, sensitivity, and utility requirements; and other considerations germane to the use of the instrument as a CEM for a bulk storage terminal. The last step was to design a laboratory test program based on the findings of the technical literature review and survey of available instrumentation. This test program was to test the instruments against the CEMS guidelines (EPA 1982, Ref. 1). These guidelines were not intended for application to benzene monitors; however, they provide general procedures and a technical approach consistent with EPA objectives in continuous emission monitoring.

LABORATORY TESTING

Based on the test plan designed in the previous phase, selected instruments were to be subjected to quality assurance (QA) testing in the controlled environment of the laboratory. Certified calibration gases of

benzene/air mixtures were to be used to define the achievable precision and accuracy of the test instruments, as well as detection limits, response time, and drift characteristics. Gas-liquid chromatography with an FID will, with judicious choice of column packing and operating conditions, permit reliable quantification of benzene in a variety of mixture types as low as the ppb range. Therefore, a GC with FID was selected as a reference method for comparison with other analyzers. The reference instrument was not considered mandatory for the laboratory testing; however, some form of confirmation analysis seemed necessary for the field testing, and the GC seemed the likely candidate. In addition to benzene/air mixtures, a test gas mixture to simulate a gasoline vapor was to be analyzed to test the ability of these instruments to detect benzene without interference from the other compounds expected in the terminal samples. The laboratory test was designed to yield a semiquantitative evaluation of analyzer performance so that the general feasibility of monitoring benzene continuously could be assessed, with the field evaluation serving as confirmation of the laboratory results. The test protocol described below was devised after the review phase was completed.

The instrument tests described below were considered desirable in carrying out the laboratory evaluations; these tests were designed from the CEM guidelines referenced above. Because some of the instruments were available for a limited time, the tests were scheduled such that the longer-duration tests were performed last to obtain the maximum amount of data in the shortest time. The low-range (0 to 10 ppm) tests were to be performed before the high range (0 to 100 ppm) tests, but this approach became moot when no usable continuous analyzers were found. In the cases where instrument availability was limited, some of the tests were curtailed. The measurement techniques to be considered during this study included the following: GC with FID, GC with PID, GC with argon ionization detector (AID), and a nondispersive infrared (NDIR) analyzer. An nondispersive ultraviolet (NDUV) analyzer was also desired, but no commercial unit was found.

Benzene Calibration Gases

A total of five different concentrations of benzene-in-air were used for each test series, corresponding to low (10 percent of full scale), medium (50 percent of full scale), and high/span (90 percent of full scale) points in the concentration ranges of interest for a continuous analyzer. The actual concentrations used were 1.114, 5.289, 9.165, 50.99, and 90.17 ppm. Hydrocarbon-free air was used as the zero gas and as the blend gas for the benzene standards.

Calibration Linearity

These tests were conducted to determine the deviation from the response predicted by a straight line between the zero and span of the instrument. As discussed in the Results section, some modification of the linearity data analysis was made. The procedure was to measure the instrument's response to zero gas and the high/span gas. Low- and medium-range standards were then introduced and the response was compared with the

predicted value. Linearity was evaluated by using least-squares linear regression with measured and predicted values as data pairs.

Response Time

This test, done coincidently with the calibration linearity test, measured the time required for the instrument to reach 95 percent of the final stable response after a step change in the input concentration. The response time test did not apply to the GCs, except the analytical cycle time was considered analogous; instead, the benzene retention time and/or analytical cycle time was recorded.

Precision (repeatability)

These tests were conducted to determine the instrument's ability to yield the same result for repeated analysis of the same sample. The procedure comprised repeated analyses of the same sample and comparison of the instrument response using the standard deviation and relative standard deviation.

Gasoline Vapor Response

The capability of the analyzers to distinguish benzene from other hydrocarbons typically found in gasoline vapor is critical to the performance of a benzene analyzer. The test mixture was a specially prepared gasoline vapor calibration standard. Preliminary test samples were also generated from the vapor space above a sample of liquid gasoline. The target concentrations were 2 to 4 volume percent total hydrocarbons and 50 to 100 ppm by volume benzene. The standard obtained from Scott Specialty Gases contained 1.99 percent by volume total hydrocarbons with 569 ppm benzene (3.41 weight percent, 2.86 volume percent of total hydrocarbon concentration). The target concentrations (2-4% total HC, 50-100 ppm benzene) were considered a good compromise between inlet-type gases (30-40% total HC, 1% benzene) and outlet-type gases (2-4% total HC, 0-50 ppm benzene). Scott, however, could not provide a certified standard meeting both criteria, so a standard with the higher concentration total hydrocarbons (2 percent) was considered a more difficult test because other aromatic and naphthenic compounds were present in significant amounts.

FIELD TESTS

In the initial stages of the project, a field test program was considered advisable to validate the results of the laboratory testing on samples taken from operating sources. The scarcity of instruments and the results of the bench testing suggested that an extensive field test was not necessary to the program objectives, so a limited evaluation of the available monitors was designed.

Test Instruments

EPA had available a number of "combustible" analyzers of the types commonly used to monitor total hydrocarbon emissions from a number of

sources. These instruments are often used on carbon absorption systems to determine when carbon-bed saturation or breakthrough has occurred and are also used to monitor potentially explosive environments as safety or warning monitors. As the lower explosive limit (LEL) for most hydrocarbons is in the range of 0.8 to 8% by volume, these units are typically designed to measure up to 5 percent by volume. Further, the instruments are nonspecific hydrocarbon analyzers and as such were expected to respond to any hydrocarbon, including benzene. There was a possibility that these units might yield a measurement indicative of benzene as a result of either high relative response to benzene or changes in exhaust benzene concentration relative to total hydrocarbons great enough to be measured by these units, so the field test was designed to verify the sensitivity as well as to verify the operation of the GC on bulk terminal emissions.

Five LEL analyzers were tested by using a heated-oven GC with a PID as the reference analyzer. Two of the instruments employed NDIR detectors, and the other three used catalytic oxidation to generate a measurement signal.

Source Selection

Several bulk terminals near Pacific Environmental Services, Inc. (PES), and EPA offices were identified as candidates for the test program. Terminals using refrigeration condensers as the vapor control device were preferred because the mechanical nature of the operation would provide more variability in the exhaust concentration. The types of petroleum products loaded through the terminal were not considered particularly germane to this study beyond ensuring that unleaded gasoline was one of the products. Table 1 summarizes the expected range of operating conditions for a typical refrigeration vapor recovery system at a bulk terminal.

Sampling System

To ensure that all instruments were measuring the identical sample and calibration gases, a sampling manifold was constructed. The manifold consisted of PVC pipe with threaded taps for the catalytic oxidation LEL sensors, tubing connectors for the NDIR units, and provisions for the GC gas sampling loop. The LEL units are normally installed with the sensor(s) directly in the gas of interest (i.e., the exhaust stack). To avoid the logistical problems of installing the sensors in the stack and, more importantly, to provide a system in which all instruments could analyze the same gas sample, the manifold shown in Figure 1 was used.

Safety requirements necessitated extracting the sample from the stack and pumping to a location at least 50 ft from the discharge point. Otherwise, all electrical equipment would have been required to meet Class I, Division I explosion-proof requirements. All of the LEL analyzers have complying sensing elements, but the indicator/controllers and the GC did not comply. Therefore, a sample was pumped from the stack to

TABLE 1. BULK TERMINAL CONDENSER EXHAUST PARAMETERS

Parameter	Minimum	Maximum
Exhaust gas flow rate, actual cubic feet/minute (acfm)	0	4,000
Exhaust gas temperatures, °F	<0	<32
Total hydrocarbons (THC), volume percent	<0.01	4.0
Benzene, ppm in exhaust	<1.0	600
Benzene, volume percent of THC	0.1	3.0

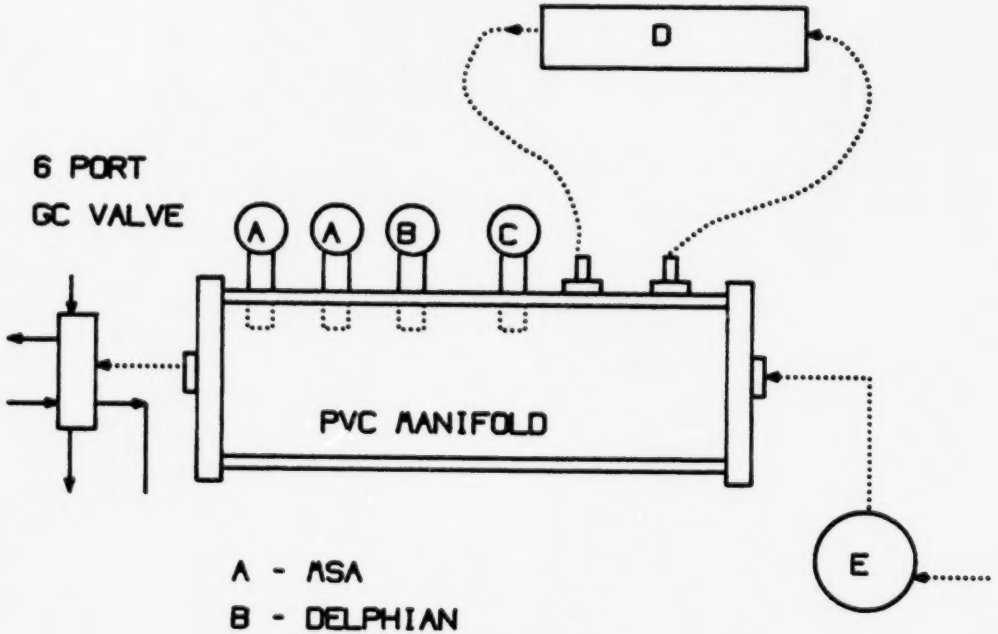


Figure 1. Sampling Manifold

the manifold located in a trailer as shown in Figure 2. This configuration permitted analysis of the same gas by all instruments. Because the exhaust gas had been cooled to -80°F in the refrigeration unit, condensation of hydrocarbons in the sample line was not a problem. A stainless steel sample line was used to maintain an earth ground for static charge dissipation. Excess sample was vented above the sampling trailer.

Analytical System

The GC was equipped with a PID, an electronic integrator, and a manually operated sampling loop continuously purged by the sampling pump. The sample extraction rate was 1 L/min to achieve a residence time (stack to manifold) of about 20 s with 1/4-in. stainless steel tubing. This configuration was intended to permit detection and quantification of benzene at a concentration as low as 0.1 ppm or as high as 100 ppm, depending on sensitivity settings. Total GC analysis time was expected to be as long as 15 min. Benzene was expected to elute in about 4 min; the appearance of higher-molecular weight aromatic compounds (e.g. ethyl benzene) eluting later than 4 min was considered possible depending on the efficiency of the refrigeration system. On the basis of the laboratory evaluation of gasoline vapor and the thermodynamics of the refrigeration system, hydrocarbon species eluting later than 10 min were not expected. For planning purposes, one GC analysis every 10 min was assumed.

The instruments evaluated and their detection methods are listed below.

Instrument	Detector(s)
Astro Model 5600	NDIR, open cell
Delphian Model 550	Catalytic oxidation/elec. resistance
General Monitors Model 580	Catalytic oxidation/elec. resistance
Horiba Model MEXA-201E	NDIR
MSA (Mine Safety Appliances) Model 510	Catalytic oxidation/elec. resistance

The MSA Model 510 and General Monitors units are dual-detector units designed for installation in carbon-bed absorbers where parallel beds are alternately used. The MSA unit provides the ability to manually read the output of each detector, whereas the General Monitors unit automatically reads the higher output from either detector. Appendix A is a list of the suppliers and their addresses.

The response time for the NDIR analyzers (Astro and Horiba) was expected to be less than 20 s. The response time for the diffusion/catalytic sensors (MSA, General Monitor, Delphian) depends on the purge rate and diffusion through the integral filters and flame arrestors; it was expected to be less than 1 min but was about 20 s with the field system. At the beginning of the field test, response time checks with calibration gas were conducted to determine the appropriate data recording times.

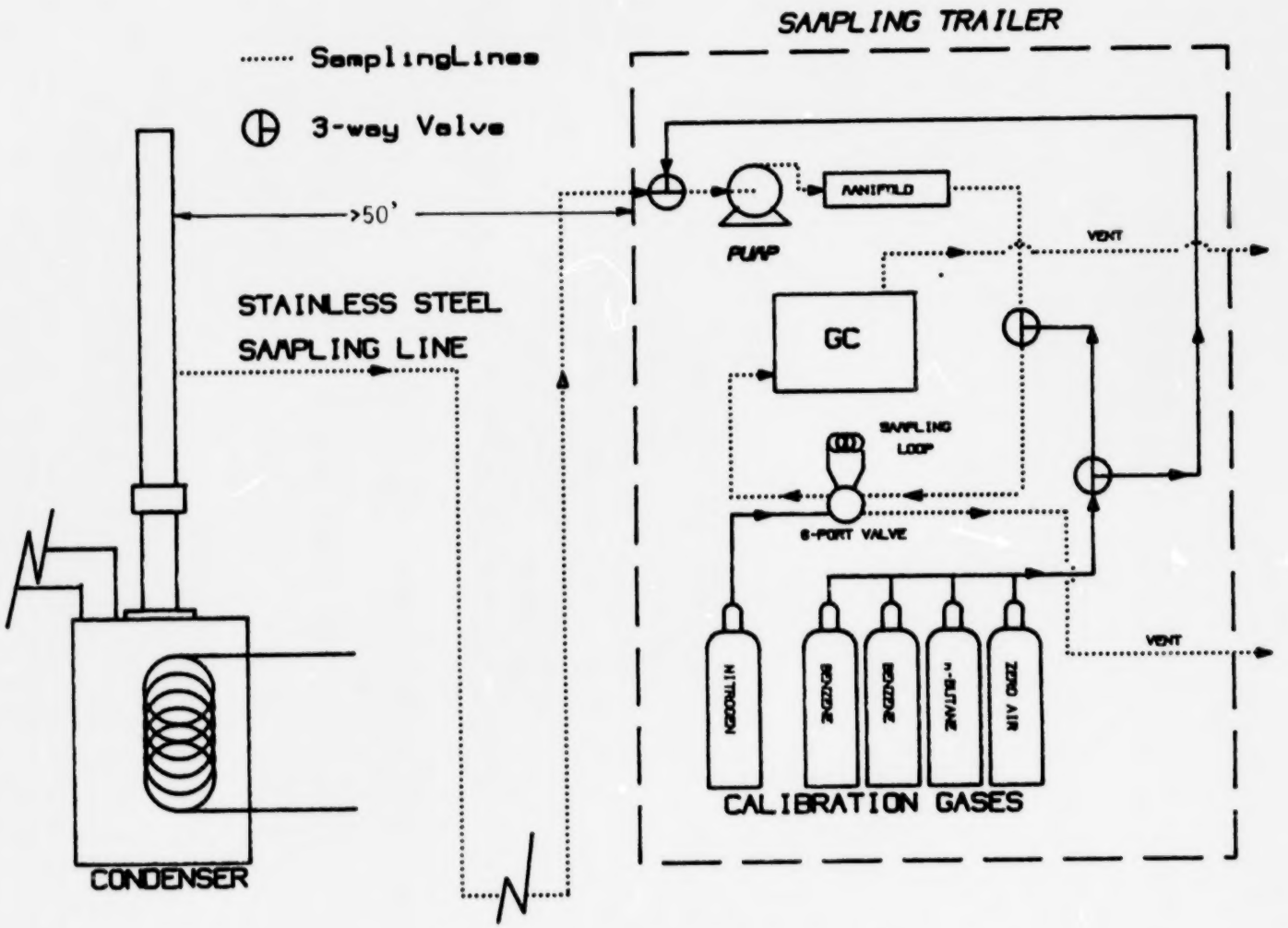


Figure 2. Sampling System

System Operation

At the beginning of each day, zero and span checks of the LEL analyzers were performed following a 30-min instrument warm-up period, along with GC analysis of the calibration gases. The GC was calibrated with benzene-in air standards and zero air. The concentration of benzene was selected from the available gases (1, 5, 9, 50, 90 ppm) to be greater than benzene concentration in the exhaust gas. The warm-up period was necessary because all instruments were shut down at night when they were unattended. During routine operations, the air in the trailer was monitored by another LEL meter to indicate if sampling should be discontinued if the hydrocarbon concentration reached 35 percent of the LEL (0.46 percent by volume; LEL of gasoline vapor is 1.3 percent by volume). This buildup did not occur.

After calibrations were completed, the sampling pump was turned on, and the sample lines were purged with stack gas. The schedule of analysis depended on loading rack activity. The objective was to analyze samples of the exhaust gas when gasoline products were being loaded, whereas loading diesel fuel was not of particular interest. When the loading rack was in more or less continuous use, analyses were made as frequently as the GC operation allowed (about every 10 min). When the loading rack was idle most of the time, a sample was taken when a truck arrived and analysis continued at 10-min intervals until no more vapors were being discharged from the stack.

Each analysis resulted in a value for benzene, a value for total chromatographable organics from the GC, and one value from each of the LEL monitors. Only one of the General Monitors and MSA sensors were used.

The LEL detectors are intended to be accurate to better than 5 percent over the range of 0 to 100 percent of the LEL. Thus, the practical limit of detection for gasoline vapor was about 0.065 percent by volume in air, which served as the lower limit for analytical comparisons.

SECTION 4

QUALITY ASSURANCE

One of the major aspects of this program is developing QA data about the instruments under investigation. Thus, QA procedures for the study were focused on the elements of precision and accuracy of the instruments. The previous section included some of the specific QA procedures used during laboratory and field testing of the instruments and described the general standards applied to the quality control (QC) checks.

Most of the tests in this study involved comparing instrument performance for analysis of standard materials rather than on actual field samples, and therefore, the study is itself a QA program. The standard materials used for calibrations are certified by the manufacturer to ± 2 percent accuracy (i.e., tag value of the gas cylinder contents was within 2 percent of the true value). Zero air and blend (dilution) air were hydrocarbon free (<0.5 ppm total hydrocarbons).

The laboratory test phase consisted of repeated analyses of these standard samples with a number of different instruments. These repeated analyses are replicate analyses of the same sample by the same lab, which is the QA guideline definition of precision (repeatability). The results section of this report contains a discussion of the QA aspects of both laboratory and field testing.

At the beginning of the field test, a series of calibration gases were analyzed on the GC to confirm its linearity and to establish response factors. Triplicate analyses of each cylinder standard were performed with a 1.0-cm^3 sampling loop. Smaller loops were available if stack gas concentrations had resulted in detector saturation. If the daily calibration response factor varied more than 20 percent from the established value, remedial action (detector cleaning, etc.) was initiated. The cylinder standards of benzene-in-air used for the laboratory evaluation were used to calibrate the GC. The LEL meters were calibrated with 0.89 percent n-butane in air (50 percent of the LEL), and a GC response factor for this gas was also generated. Dynamic zero was set by using zero air with <0.5 ppm total hydrocarbons. The calibrations were normally conducted by flowing calibration gas through the manifold; system response and response time checks were conducted at the outset by flowing the gases through the entire sampling system. Daily calibrations were done prior to and at the conclusion of the day's sampling.

SECTION 5

RESULTS AND DISCUSSION

GENERAL

This section is divided into three major subsections: literature review, laboratory testing, and field testing. Each of these subsections describes the significant actions performed, results of the investigations, and discussion of the significant findings in terms of the experimental objectives and conduct.

LITERATURE REVIEW

The literature review consisted of searching in-house and EPA library reference documents, technical journals, and personal contacts for pertinent information regarding analysis of benzene vapor in a variety of media (References 2-20). The 20 different techniques for detection of benzene that were identified are listed in Table 2. The techniques were divided, somewhat arbitrarily, into categories of high, medium, and low probability for successful application as continuous benzene monitors, so subsequent effort and investigation could be concentrated on the high-probability systems.

The theory (and practice) of organic compound analysis suggests that because benzene is sufficiently distinct from any other organic compound, analysis for benzene is relatively simple, though not necessarily easy, with a knowledge of the nature of the carbon-hydrogen (C-H) and carbon-carbon (C-C) bonds and carbon-hydrogen ratio. However, the instrumentation typically used in organic chemistry analysis is generally not suitable for field applications and is usually designed for single sample analysis. Many, if not most, of the CEMs in use today had their start in single-sample laboratory analytical methods, evolving through use as analyzers for automated processing of multiple discrete samples into continuous analyzers. This appears to be the course for development of a benzene CEM.

Analyzers based on FIDs have been the most prominent among those used for measurement of hydrocarbons, either with or without a GC. The detector itself measures the ionization resulting from burning a molecule in a hydrogen flame and is particularly sensitive to the C-H bond dissociation; it does not specifically detect any given compound or class of compound. Preceding the detector with some means of time separation of analytes (e.g., a chromatograph) permits identification of analytes by time differences and quantification by the FID electrometer.

TABLE 2. POTENTIAL BENZENE ANALYTICAL METHODS

Technique	Description
Gas chromatography	
With PID	High potential, organic analytes
With FID	High potential, organic analytes
Nondispersive ultraviolet	High potential, organic/inorganic analytes
Nondispersive infrared(NDIR)	Medium potential, organic/inorganic analytes
Tunable atomic line molecular spectroscopy	Medium potential, numerous analytes
Photoionization	Low potential, organic analytes
Other techniques investigated demonstrating low potential	
Electrocatalytic	Not specific
Mass spectroscopy	Not suitable for field instrument
GC with FPD, ECD, TCD*	Less sensitive than FIDs or PIDs
Fluorescence	No response for benzene
Chemiluminescence	No response for benzene
Coulometric	Measures sulfur, halogens, nitrogen
NDIR-gas filter correlation	Interferences
Colorimetry	No convenient benzene reactions
Paramagnetic, Thermal conductivity, Electrochemical, Flame photometric	Either not specific or no response

*FPD-flame photometric detector, ECD-electron capture detector, TCD-thermal conductivity detector.

PIDs offer some degree of specificity through selection of the energy output of the ultraviolet (UV) lamp used to generate the ionizing radiation. Different organic compounds have different ionization potentials (IPs), although the differences are more apparent between homologous series than between compounds within a homologous series. Benzene, for example, has an IP of 9.25 electron-volts (eV), while aliphatic hydrocarbons have IPs in the range of 9.8 to >12.0 eV. Thus, a 9.7-eV lamp will ionize benzene but not aliphatic compounds, and is semispecific. When a PID is used with a GC, compound identification and quantification can sometimes be enhanced by the partial selectivity of the detector.

A GC with both FID and PID was selected for laboratory testing for several reasons. First, the GC/FID was known to yield accurate results over a wide range of concentrations, and calculation of detector sensitivity showed sufficient resolution for this study. The literature suggested that benzene could be chromatographically separated from other expected components with a fairly short packed column to achieve reasonable batch analysis times. The PID was selected to evaluate the benefits of selectivity when combined with a GC. Further, the PID does not require the utilities (hydrogen, air) required by the FID and is simpler to operate, which are important features for a field instrument.

Photometric analysis is possible because the benzene molecule will absorb both IR and UV radiation at characteristic wavelengths and the absorption characteristics can be used to both identify and quantify benzene in a sample, providing interfering compounds can be eliminated or otherwise ignored (i.e., mathematically). The problem, especially with IR analysis, is that many other organic compounds absorb in the same region and similar compounds may have absorption peaks at virtually the same wavelength as benzene. The higher photoelectric energy required for the shorter UV wavelengths tends to result in stronger absorption bands and can more easily provide an absorption fingerprint. However, both techniques require consideration of the entire absorption pattern and whether any other absorption is interfering. Use of UV spectra offers some promise for several reasons:

- Benzene shows a very strong peak at ~180 nm and secondary peaks at ~200 and ~225 nm.
- Other aromatic compounds (e.g., toluene) do not show the 180-nm peak, but do show the 200- and 225-nm peaks, although usually shifted up slightly from the benzene peaks.
- Alkanes show no UV absorption at wavelengths greater than 160 nm.
- Vapor-phase analysis permits identification of fine peaks not readily apparent in liquid (solvent) media.

Potential interferences are unsaturated hydrocarbons, many of which exhibit peaks over the range of 150 to 300 nm, and data on vapor composition of bulk terminal emission shows the presence of a large number of branched-chain and cyclical alkenes. Because there is no commercial monitor avail-

able, the practicality of an NDUV instrument for benzene measurements at bulk storage terminals is unknown. In general, the UV absorption bands, although stronger than infrared, are much broader. This is a disadvantage for identification, but an advantage for quantification, especially for low-concentration, vapor-phase analysis.

NDIR analyzers are available for both liquid- and vapor-phase measurement. Manufacturers have indicated that benzene could be detected and quantified with IR analysis. Our experience with these NDIRs suggested that reliable identification of benzene and subsequent quantification would require a fairly detailed IR scan of the sample and mathematical equation solving. Together, these operations are sufficiently time-consuming (on the order of several minutes) to make the instrument a batch analyzer rather than a continuous one. However, the IR instrument was considered a possibility and was included in the design of the laboratory experiments.

Other techniques investigated that showed limited promise include tunable atomic line molecular spectroscopy (TALMS) and the collection of samples on solid sorbents with subsequent desorption and analysis by using GC and a variety of detectors. Several other techniques, including most of those used for stack and ambient monitors demonstrated low potential, either because they would not work for organic compounds or because there was no evidence to suggest their feasibility.

LABORATORY TESTING

Experimental Conditions

Instruments Tested --

A total of five separate instrument configurations were evaluated during the laboratory testing phase of this project. The MIRAN 1A NDIR analyzer, manufactured by Foxboro, was the only unit with the capability to operate in a continuous analysis mode. The other instruments were the HNU 301, a mid-sized, laboratory-type GC equipped with a temperature-programmable oven and FID and PID detectors, manufactured by HNU Systems; the Scentor, a portable, heated-oven GC with an AID, by Sentex; and the Photovac 10S50, a portable, ambient-temperature GC with PID, by Photovac International.

The HNU unit was used in the dual-detector configuration with the PID (nondestructive) followed serially by the FID (destructive). A single-channel integrator was used for one detector, and the other was monitored with a strip-chart recorder. The operating characteristics of the FID were well-known and known to be adequate for the purposes of this experiment; thus the FID was used to establish the basic operating parameters for the chromatograph. Carrier gas flow rate, column types and lengths, oven temperatures (isothermal or programmed), and output sensitivity/attenuation were the characteristics of interest. The characteristics of the PID were not so well known, so the initial tests were conducted with the output of the PID connected to a chart recorder to semi-quantitatively compare the response of the PID to FID and to subjectively observe noise

level, signal-to-noise ratio, absolute signal level, and zero drift. This instrument was used in a manual-injection mode by extracting samples from a purged manifold and injecting the sample into the GC with a gas-tight syringe.

The column used for the HNU GC was 35 percent BC-150 on 100/120 mesh Chromosorb P-AW. This column was recommended by several suppliers of chromatography supplies because it passes aliphatic hydrocarbons very quickly while retarding the elution of aromatic compounds. Benzene is the first aromatic compound to elute with this column. Similar columns were used for the portable units, by using the same liquid phase (tris-(2-cyanoethoxy)-propane) at lower concentrations (10 percent). After some experimentation, an oven temperature of 115 to 120°C with a carrier gas (nitrogen) flow rate of 30 to 35 mL/min were selected as operating conditions. At these conditions, benzene typically eluted at 3.10 to 3.50 mins, followed by toluene at about 4.2 min. Higher column temperatures result in excessive column bleed, in part because of the high concentration (35 percent) of the liquid phase on the packing. The HNU column was a 1/8-in. by 10-ft. stainless steel coil, whereas the portable units had 1/8-in Teflon® columns.

The MIRAN 1A unit was set up with a continuous-flow sample line purging the spectrophotometer cell and operated in both the wavelength scan and fixed wavelength modes with a path length of 20 m. The system was purged with the sample to be analyzed until the absorbance at 9.9 μm stabilized, when the purge was discontinued, and the bandwidth scans and single range analysis results were obtained.

The Scentor portable GC was supplied with a column recommended by the manufacturer (a 1/8-in. by 6-ft. Teflon® column with tris-(2-cyanoethoxy)-propane on 80/100 Chromosorb P-AW) and was used as configured by them. The unit was set up with an internal sample pump and operated with a gas sample preconcentrator (an absorption/desorption column). Sample size was varied by changing the length of time sample was delivered to the sampling column. After sampling, this column was thermally desorbed onto the analytical column. The analytical column was kept in a heated oven (isothermal operation), and compounds were identified by retention time by using the internal microprocessor. The unit was supplied with an AID for detection and quantification of the analytes. The AID uses excited-state argon as a medium to transport ions to the sample by ionizing argon and detecting the ionized organic molecules resulting from argon-sample collisions. The operating characteristics are similar to the PID in that the excited-state argon atoms have an energy state of about 11.6 eV and thus will ionize compounds with IPs of less than 11.6 eV. The particular unit that was available to us was set up for detection of ppb-range organic compounds, creating some difficulties, as discussed in this section under Results.

The portable Photovac instrument was made available in its optional configuration with the microprocessor/plotter module for instrument control and data reduction, equipped with a PID, manual injection ports, an on-board sample pump, and a Teflon -tubing packed column for ambient temper-

ature operation. The Photovac operates only at ambient temperature and accomplishes separation by programmed operation of the sample flow valves and use of a split column to minimize the analysis cycle and eliminate solvent and late-eluting peaks. The column is split into a 6-in. section and a 48-in. section (replacing the more common precolumn/analytical column arrangement) so the front section can be backflushed quickly for removal of long-eluting components. Column packing for these experiments was tris-(2-cyanoethoxy)-propane on 80/100 Chromosorb P-AW, also used in the Scentor GC instrument.

Sample Types --

Two sample types were used in the laboratory testing: cylinder gases containing various concentrations of benzene blended with hydrocarbon-free air; and cylinder gases containing a custom-made standard of gasoline vapor in air. The calibration gases were obtained from Scott Specialty Gases (Plumsteadville, PA) and the benzene cylinders were certified materials with a 2 percent analytical accuracy; the gasoline vapor sample required a special procedure and was supplied with a GC capillary column analysis of its components. It was anticipated that the composition of the field samples would depend on the control device used. The efficiency of refrigeration and carbon adsorption systems generally increases with increasing molecular weight so the outlet gases tend have a higher mole fraction of low-molecular weight (higher volatility) compounds than the inlet gases. The efficiency of thermal oxidizers is not significantly affected by volatility, so the outlet and inlet gases tend to have the same relative composition. To test the analytical systems, the gasoline vapor sample represented uncontrolled vapor products rather than the emissions at the outlet of a refrigeration system. The gasoline vapor sample was supplied in a low-pressure cylinder (30 psi) because condensation of some of the less volatile components will occur at higher pressures. The dew point of the mixture was estimated by Scott to be about 50°F at 30 psi. Because the ambient temperature in the laboratory ranged from 65 to 70°F, some condensation may have occurred, changing the composition of the vapor somewhat.

Results

For purposes of the GC analysis, evaluations of analytical system response were performed by using the product of concentration and injection volume (ppm·μL) to calculate the "relative mass" of analyte delivered to the detector. Some error is introduced by ignoring changes in ambient pressure and temperature, but the maximum daily variation in pressure and temperature observed was 0.5 in.Hg and 5°F, respectively. This daily variation would not cause errors greater than 2 percent. Over the course of the laboratory testing, variations of 1.0 in.Hg and 10°F could account for ~5 percent difference between the calculated relative mass and the true mass and these variations could also account for some of the observed day-to-day variance in the response factors. Typical GC analysis would include an internal or external calibration at least daily, and the portable GCs tested could be programmed to perform such a calibration as frequently as every other analytical cycle.

Summaries of the laboratory data are included in Appendix B. These summaries are derived from the printed output from the printer or plotter device used for the individual instruments. Example outputs from the instruments are included in Appendix C.

GC/FID/Heated oven --

In general, the FID performed well, as expected. The response was linear over the entire range of sample concentrations of interest (1 to 100 ppm), though the calibration curves show some day-to-day variation and some deviation from linearity. A linear regression analysis was chosen instead of the QA guideline mid-scale deviation because the linear regression offers information useful for extrapolating and interpolating results to other concentration ranges. Least-squares linear regressions calculated for the daily analytical results yielded correlation coefficients ranging from 0.9441 to 0.9998, averaging 0.98. The intercept of the linear calibration lines averaged -53 ppm·μL, ranging from -33 to +104 ppm·μL. The standard error of estimate (predicted value) from the linear regression calculations ranged from 24 ppm·μL to 600 ppm·μL, averaging 229 ppm·μL. Figure 3 compares the true value with the linear regression predictions over the course of the laboratory testing and shows that the system response is linear. As described below, the manual syringe injection technique is probably responsible for most of the observed daily variations. The manufacturer states that the linear range of the FID is 2,000,000 and that the minimum detectable quantity of benzene is 100 pg. A 100-μL injection of 1 ppm benzene contained ~350 pg and was readily detected. With a 100-μL injection of 100 ppm as full scale, the GC/FID yielded accuracy and a minimum detection limit of ~2 percent of full scale with the operating parameters of the detector and integrator optimized for measurement in the 20-ppm range. A typical operation as a gas analyzer would have a sample loop of 0.25 to 1.0 cm^3 (250 to 1000 μL), so detection of 1 ppm would be readily achievable, given the reported sensitivity and the experimental linearity data.

To evaluate the precision of the system, replicate analyses were compared by using both the relative standard deviation (RSD) and the absolute standard deviation as measures of repeatability. The relative deviation will be constant if the variance is proportional to the magnitude of the sample value (for example, a leak in the injection syringe proportional to volume injected); the absolute deviation will be constant if the variance is independent of the magnitude of the sample value (the baseline noise level of the detector). Usually, both types of variance are present to some degree. Figure 4 shows the distribution of the replicate analysis RSDs as (a) a cumulative distribution plot and (b) a frequency histogram. The cumulative distribution shows that 95 percent of the values were less than 50 percent RSD. The histogram suggests a lognormal distribution and that the arithmetic average RSD (13.77 percent) is biased high by a few anomalously high RSD values. The experimental design was such that the value of the absolute deviations in instrument response cannot be compared directly because of changing sensitivities, attenuation, and other operating parameters. To evaluate the absolute deviations over the duration of the testing, the individual responses were used to calculate relative mass by using the daily regression equations.

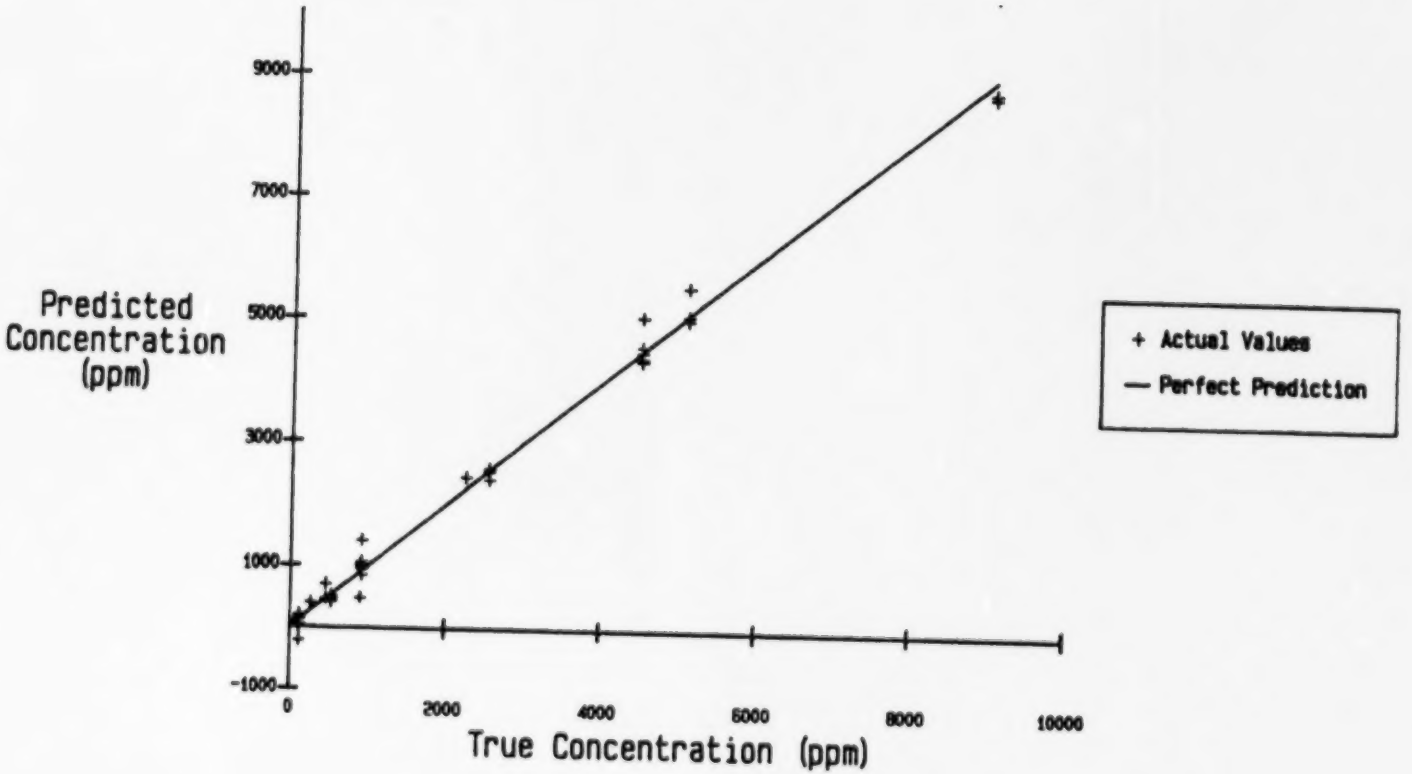


Figure 3. FID Calibration Linearity

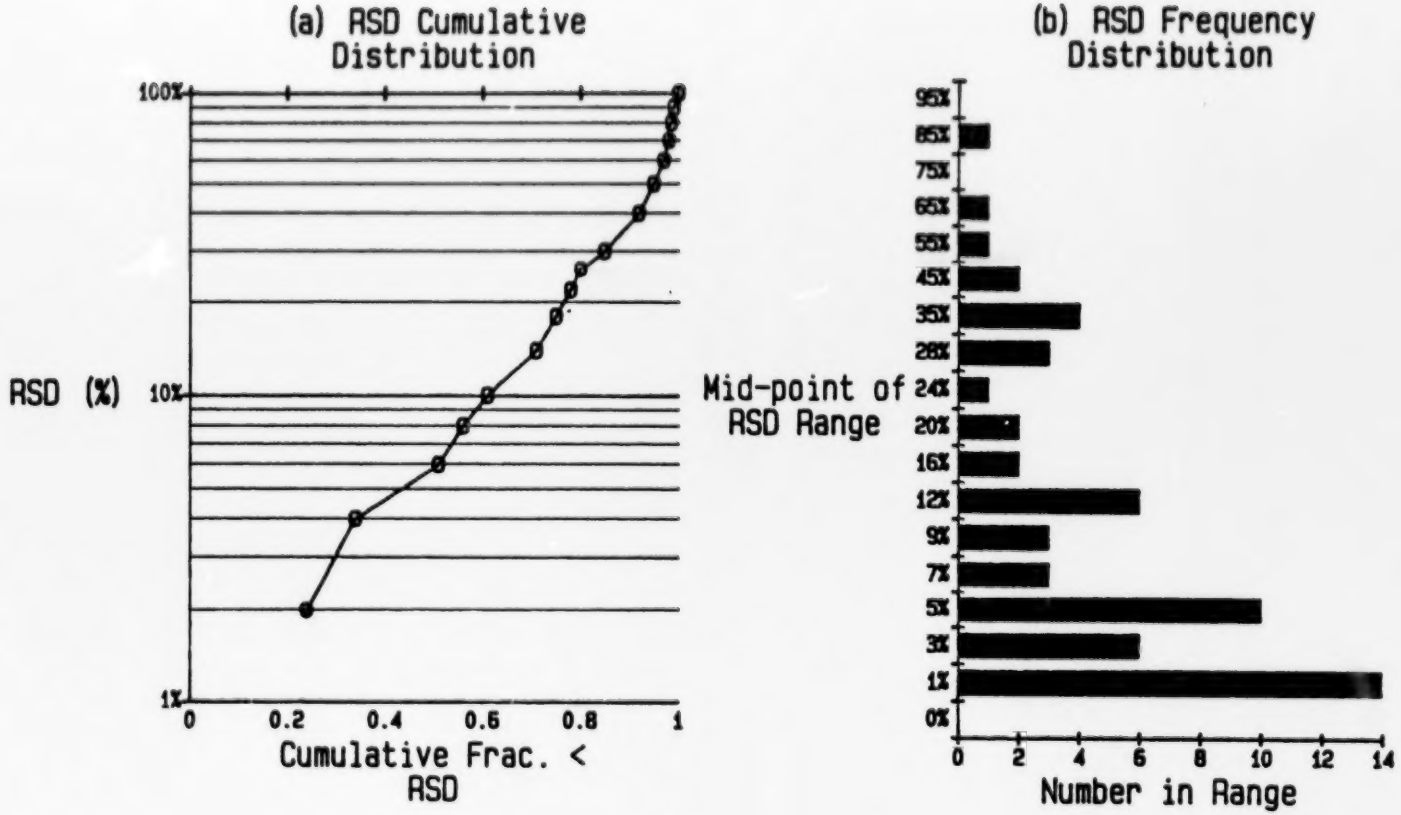


Figure 4. FID Replicate Analysis

When used to analyze the gasoline vapor standard, detector performance was consistent with performance on the benzene standards. Table 3 presents the results of replicate analyses of the gasoline vapor standard. The chromatograph operating conditions provided good separation of the benzene peak as seen in Figure 5. These data show a repeatability comparable to that obtained on the benzene-in-air standards in terms of the relative amount of benzene present in the standard; however, the benzene concentration predicted by linear regression shows more variability than would be expected. This may be a result of the dew-point concern mentioned earlier. However, the absolute value of the benzene concentration in the gasoline vapor sample was not the primary concern of this experiment; the ability of the GC/detector to distinguish and quantify benzene from the mixture was the objective. The relative FID response to most hydrocarbons is nearly constant as it measures the first ionization of the C-H bond and acts as a "carbon counter." Because of this property, FID analysis of a paraffinic/aromatic/naphthenic hydrocarbon mixture yields individual component results very nearly proportional to the weight fraction of the components in the mixture. The analysis of the gasoline vapor standard showed the benzene concentration to be 3.28 percent by weight. The average value of 16 analyses of the benzene fraction of the chromatographed samples was 3.23 percent, with a standard deviation of 0.90 percent.

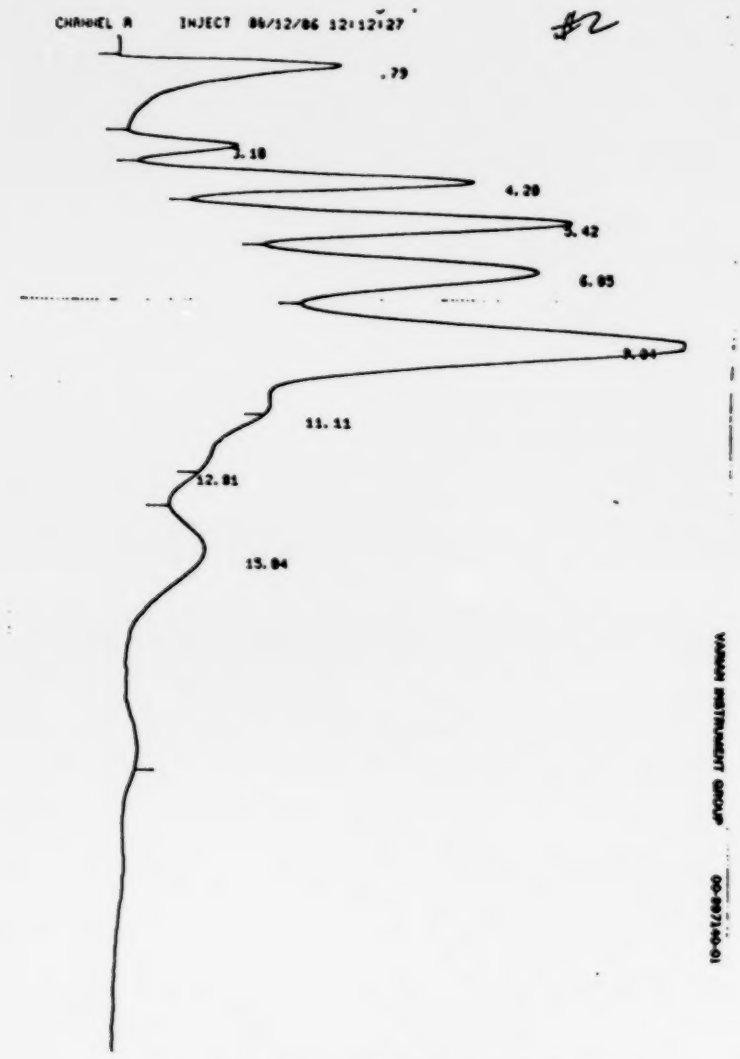
GC/PID/Heated Oven --

The precision and accuracy of the PID performance was very similar to that of the FID. The linear regression performed for the multipoint calibrations shows strong linearity in that correlation coefficients ranged from 0.946 to 0.999, averaging 0.984. The standard error of estimate for the predicted values ranged from 82.8 to 738 and averaged 283 ppm·μL. These values, like those for the FID, were determined by using the average response to replicate injections of each calibration standard. If the results of each individual injection had been used for the regression calculations, the resulting correlation parameters would have evidenced the variability of the replicate analyses. If the individual responses were used, the standard error of estimate and slope error would increase and the correlation coefficients would be lower, but the slope and intercept values would not change significantly. Use of the average response data is more indicative of the linearity of the system, whereas the individual value data suggest that significant error can be expected if a single analysis is used for determining concentration. As mentioned above, this variability seems to come from the manual injection of sample, because the values of the various statistics are virtually the same for both PID and FID, and they appear to be independent of detector or chromatograph operating conditions. Figure 6 displays a comparison of the perfect prediction line (100 percent linear) with the actual data (predicted value versus true value). Figure 7 shows the replicate analysis data as (a) a cumulative distribution and (b) a frequency histogram. The data exhibit the same characteristics as the FID data.

No significant differences in precision and accuracy were observed between PID lamps of different ionization energies. The only difference observed was a lower relative response factor for the lower-energy lamp (9.5 eV vs. 10.2 eV), as expected. The relative response for the 9.5-eV

TABLE 3. FID ANALYSIS OF GASOLINE VAPOR

Date	Predicted Concentration, ppm (linear regression) Benzene	Total	Benzene, % of total Response
	113	3,910	2.73
August 1	67	2,980	2.03
	80	2,710	2.74
Average	87	3,200	2.50
Standard Deviation	19	510	0.33
August 6	146	4,620	3.50
	228	5,390	4.52
Average	187	5,000	4.01
Standard Deviation	41	390	0.51
	79	2,860	3.32
August 8	114	3,420	3.80
	86	2,520	4.04
	90	2,520	4.23
Average	92	2,830	3.85
Standard Deviation	13	370	0.34
	128	2,510	2.55
August 12	120	2,350	2.55
	89	1,640	2.70
Average	112	2,170	2.60
Standard Deviation	17	380	0.07
	128	2,510	5.08
August 15	160	4,720	3.38
	143	7,000	2.04
	175	6,960	2.51
Average	151	5,300	3.25
Standard Deviation	18	1,860	1.16



1 00/12/86 12:12:27 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 41 INDEX 41

PEAK#	AREA%	RT	AREA	BC
1	5.787	0.79	228007	02
2	2.041	3.10	80424	02
3	7.749	4.2	305333	02
4	13.545	5.42	533694	02
5	18.346	6.85	722847	02
6	38.141	9.04	1502806	02
7	6.356	11.11	250444	02
8	1.941	12.81	76473	02
9	6.093	15.04	240083	03
TOTAL	100.		3940111	

Figure 5. Gasoline Vapor Chromatogram
HNU Example

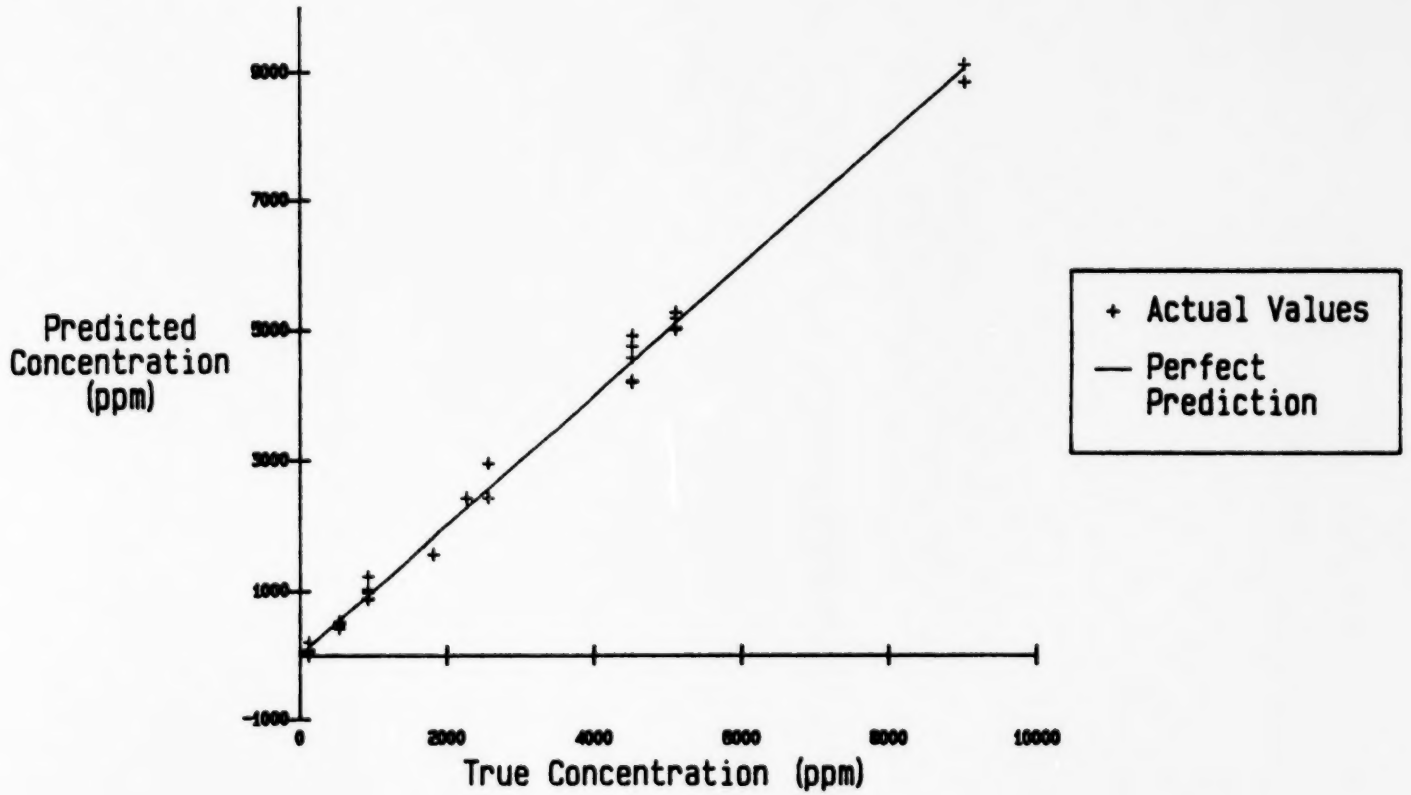


Figure 6. PID Calibration Linearity

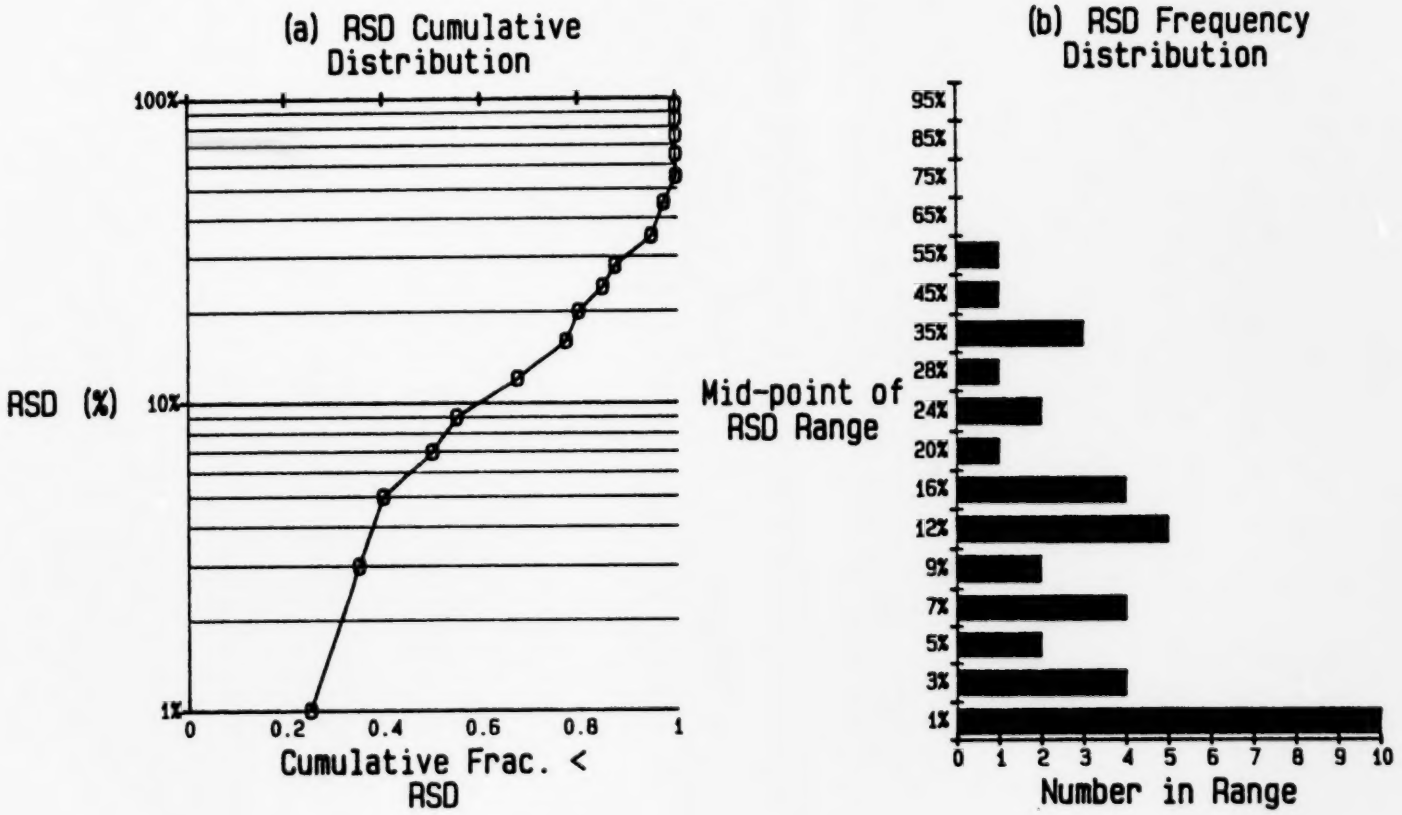


Figure 7. PID Replicate Analysis

lamp was approximately half of that for the 10.2-eV lamp, which would increase the lower limit of detection compared to the higher-energy lamp if all other conditions were the same. As with the FID, the lower limit of reliable detection is about 2 ppm·μL and would increase to 4 with the 9.5-eV lamp. However, a GC/PID system optimized for bulk terminal monitoring would have a dedicated gas sampling system, column selection, and operating conditions and would likely achieve a sensitivity of 0.1 ppm or lower by increasing sample size, flow rate, etc. The benefit of using the lower energy lamp is a reduced response to aliphatic hydrocarbons, most of which have IPs greater than 9.5 eV and do not ionize. Some increase in sensitivity could probably be realized as a result of reduced detector response to any aliphatic compounds coeluting with benzene. This was confirmed during the field tests.

For the most part, PID analysis of the gasoline vapor standard produced the expected results. Because there are compounds in the mixture with IPs greater than 10.2 eV that will not be detected, the total mass detected will be lower than detected with the FID; thus, the calculated benzene fraction of the total would be higher than the true (FID) value. The average benzene fraction of the total response was 4.96 percent, with a standard deviation of 4.14 percent. Although the average value is consistent with expectations, the deviation is considerably higher than that obtained with the FID. The data in Table 4 show that the predicted concentrations are relatively precise (average = 174 ppm, standard deviation = 26.1 ppm) and that the high deviation in percent benzene comes from two analyses where the benzene value was comparable to that in other analyses, but the total response was significantly lower than expected.

GC/AID/Heated Oven --

As mentioned previously, the portable Scentor unit obtained for testing was built for ppb-level measurements (ambient) and the unit was available only for a short period of time. The high concentrations being tested prevented obtaining any reliable quantification data. Limited success was obtained with the 1-ppm benzene-in-air standard, but no attempt was made to analyze the gasoline vapor standard because of the failure with benzene standards. The unit did not have provisions for manual injection, and the minimum sample time with the on-board pump was 1 second, which still delivered too much sample to the analytical system for our purposes. The unit may well be capable of the necessary separation and detection, but no data were obtained to support such a conclusion.

GC/PID/Ambient Oven --

The test unit for this configuration was a Photovac Model 10S50 portable GC with PID and ambient temperature oven. It was initially thought that ambient operation would not adequately separate benzene from the other components of gasoline vapor. However, the "tris" column and appropriate programming of the flow control valves permitted an adequate separation. The ability to separate benzene from the other components was determined before the evaluation tests were begun. The unit offered the capability for automatic calibration with an external gas standard and could be programmed to calibrate after a set number of sample analyses. This feature was used to compensate for retention time drift caused by

TABLE 4. PID ANALYSIS OF GASOLINE VAPOR

Date	Predicted Concentration, ppm (linear regression)		Benzene, % of total Response
	Benzene	Total	
	186	1,700	11.15
August 1	208	1,770	11.92
	184	3,450	5.45
Average	193	2,310	9.51
Standard Deviation	11	810	2.88
	124	7,330	1.97
August 12	168	9,270	2.04
	161	9,410	1.94
	176	8,940	2.20
Average	157	8,740	2.04
Standard Deviation	20	830	0.10

changing room temperature and detector variations over time. The procedure used for sample analysis was to connect a cylinder of one of the benzene standards to the calibration gas port and use the on-board sample pump to withdraw a sample from a Tedlar® bag. The same nitrogen used for the HNU unit was used for the Photovac GC. The unit was available for only a limited time so the test program was modified to obtain the most information within the time allotted. The control program for the unit also permitted a variety of results reporting, including an integrated area count as well as calculated concentrations determined by internal or external calibration data. Most of the tests were conducted by using the direct concentration calculation mode, with the most recent calibration standard analysis as a reference. This approach does not permit much evaluation of detector variations (zero drift, sensitivity, noise, etc.); however, the manufacturer stated that the unit was built to compensate for these variations rather than include complicated (and heavy) temperature and electrical control mechanisms.

The unit was evaluated both with manual injections of benzene standards and with pumped samples from a Tedlar® bag. A number of trials were necessary to get the machine programmed to calculate and report the results as desired; however, usable data, if not the desired data, were obtained most of the time. As a check on the reported results, the plotted peak heights at particular detector gain settings were measured for comparison among data reported in parts per million or volt-seconds. Figure 8 shows the Photovac linearity data in the same format as was used to report the HNU unit data. This plot shows distinct biases at the upper and lower ends of the regression line in the form of overestimation at the low concentrations and underestimation at the higher concentrations. It appears that the internal volume of the analytical system was large enough compared to the sample volume so that a measurable amount of the previous sample remained in the system. Succeeding analyses of identical samples gave results closer to the true value. If the concentration of the calibration gas was higher than the sample gas, then the first analysis of the sample would be the highest and would decline with succeeding analyses of the sample. Conversely, a sample gas concentration higher than the calibration gas value meant that succeeding sample analyses would yield higher results. The unit was not available long enough to test this hypothesis rigorously or to determine a remedy.

The unit was not available long enough to perform rigorous tests on its ability to quantify benzene in gasoline vapor, although a few tests were conducted to ensure that it could be done. Figure 9 displays copies of chromatograms from this unit. The benzene peak is no. 15, eluting at about 310 s. Two replicate analyses gave results of 206.8 and 212.5 ppm benzene. These agree well with the HNU PID results and are consistent with the repeatability of the benzene-in-air standards.

NDIR --

The NDIR analyzer was able to quantify the benzene-in-air standards reasonably well, but could not distinguish benzene from the rest of the components in the gasoline vapor mixture.

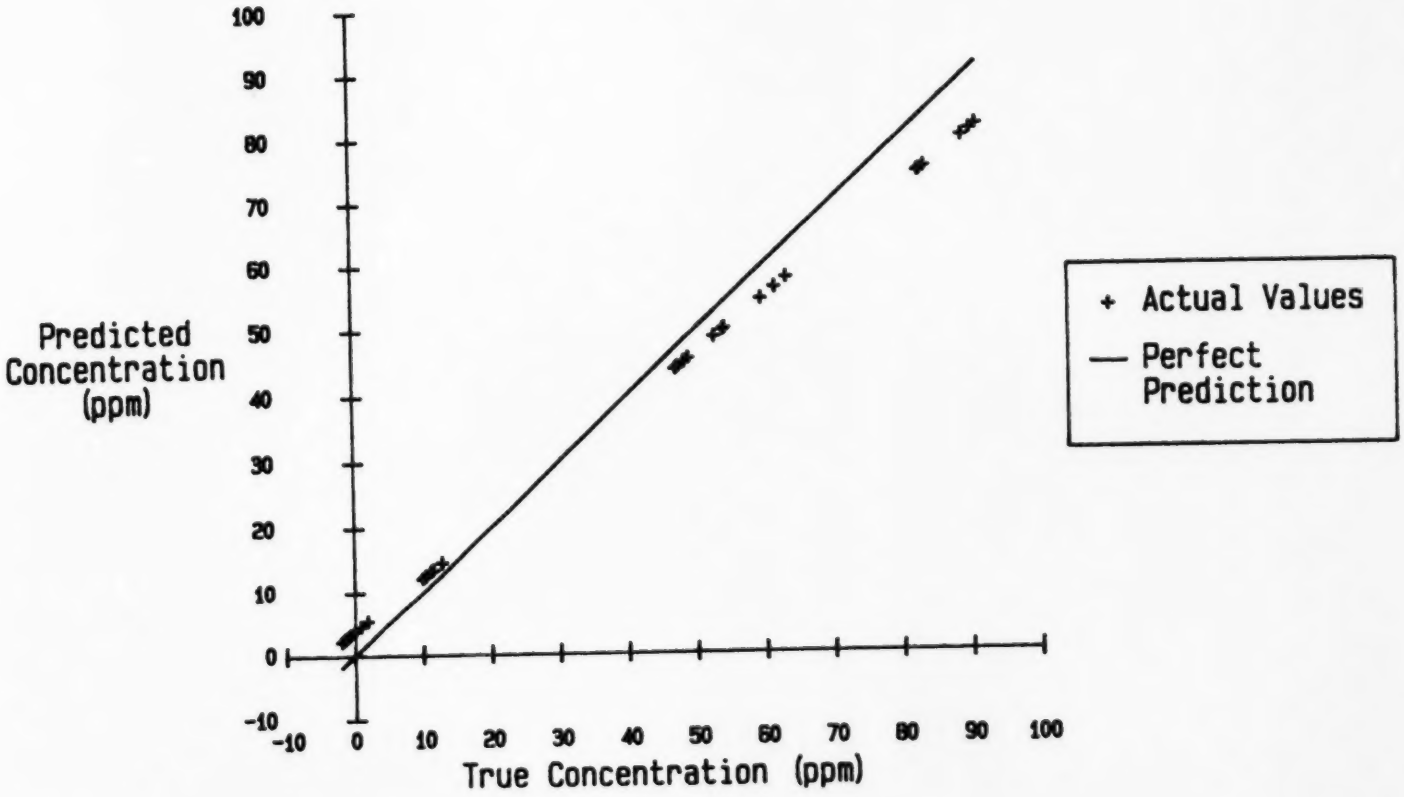


Figure 8. Photovac Calibration Linearity

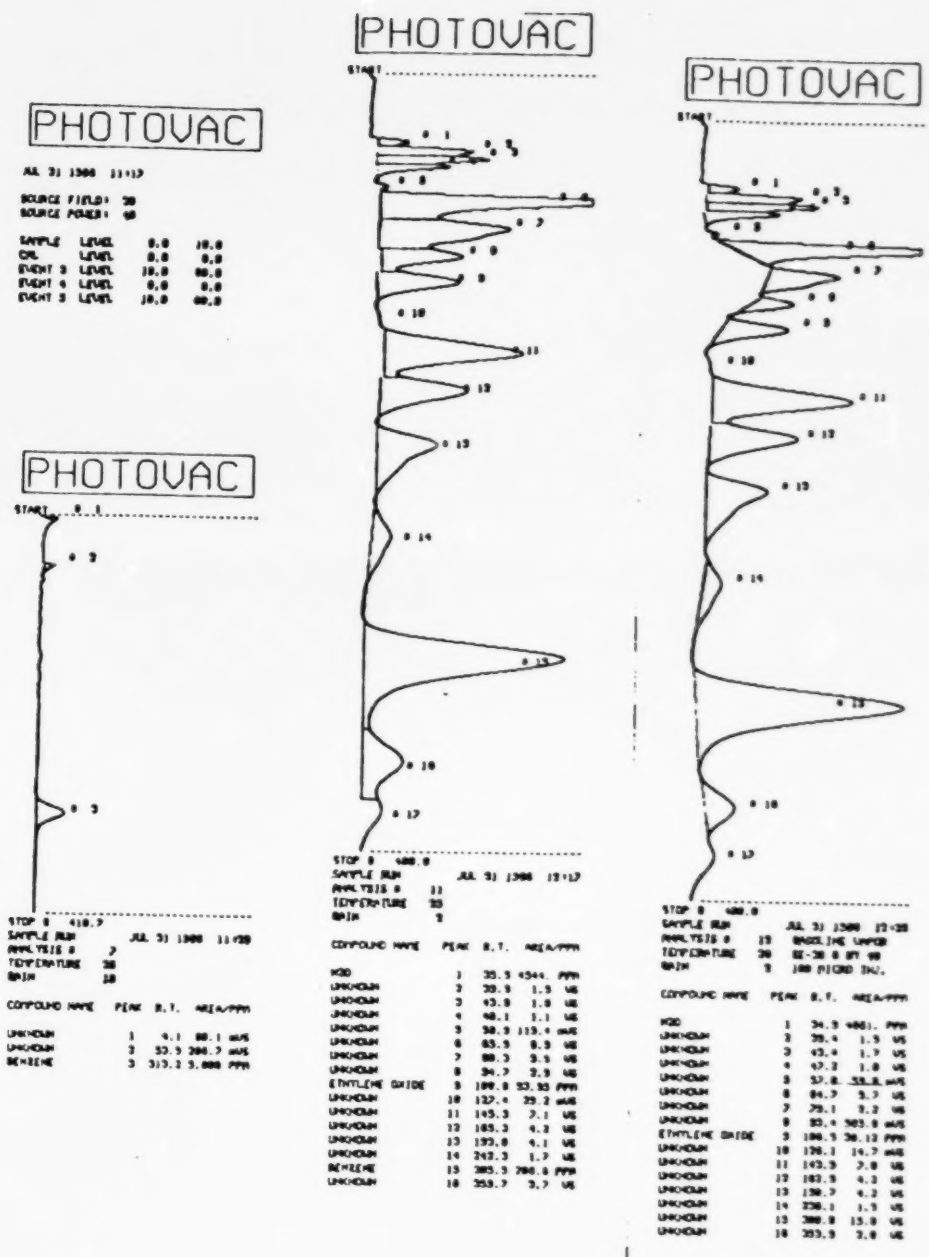


Figure 9. Gasoline Vapor Chromatograms
Photovac Examples

FIELD TESTING

The laboratory testing and literature review showed that there was no commercial instrument to continuously monitor benzene in gasoline vapors. However, the testing showed that GC analysis would likely be practical for quantification with reasonable analytical cycle times. Further, a number of terminal operators were known to use explosimeters, or LEL analyzers, to monitor the status of carbon-bed absorbers. Thus a limited field test of the practicality of GC analysis was conducted to verify the laboratory testing; the field test also provided a means to evaluate the feasibility of using the LEL "total hydrocarbon" analyzers as surrogate benzene monitors. Table 5 lists the LEL instruments involved in the field test.

Field Test Description

Analyzers --

The instruments tested were five LEL analyzers and the HNU GC/PID as used in the laboratory testing with the addition of a gas sampling loop. Of the five LEL units, three used catalytic-oxidation sensors for hydrocarbon detection and two used NDIR detectors.

Sampling System --

The facility safety requirements necessitated extracting the sample from the stack and pumping to a location at least 50 ft from the discharge point, as previously shown in Figure 2. This configuration permitted analysis of the same gas by all instruments. A stainless steel sample line was used to maintain an earth ground for static charge dissipation. Excess sample was vented above the sampling trailer. A sample extraction rate of 1 L/min was used to achieve a residence time (stack to manifold) of about 20 s. Dilution of the stack gas was necessary for both inlet and outlet samples to maintain on-scale reading for the LEL analyzers.

Gasoline Bulk Storage Terminal Operations --

The terminal used for the tests was Mobil Oil's Baltimore plant, supplying three grades of gasoline, two grades of diesel fuel, and heating oil, which were loaded into tank trucks through a 5-bay loading rack. Operation was around the clock, but activity was concentrated from 7:00 a.m. to 3:00 p.m. The terminal was accessible to us only during the regular day-shift work hours. Displacement of tank-truck vapors during loading forced vapor through the refrigeration system, so discharges to the atmosphere occur only when a tanker was being loaded. Because of the volume of the vapor collection system, no certain method could determine whether the discharged vapors came from a gasoline tanker or a diesel tanker. Samples were taken only when vapors were being discharged.

Field Test Results

General --

Two of the LEL analyzers did not work properly and one did not work at all. As a result, there are no data for the Delphian catalytic oxi-

TABLE 5. FIELD TEST LEL ANALYZERS

Make	Model	Type
MSA	511	Dual Head Combustible Gas Detection System w/sensors
Astro	5600	Combustible Gas Monitor w/sensor
General Monitors	980	Dual Channel Combustible Gas Monitor w/sensors
Horiba	Mexa 201E	IR Hydrocarbon Analyzer
Delphian	550	Hydrocarbon Detector with sensor

dation unit, and IR source problems for the Horiba NDIR unit resulted in greatly reduced response but still permitted some evaluation of its performance. A total of 40 GC analyses were made over the 4-day test period. Fifty analyses were made with each of the four LEL analyzers. Because the discharge from the stack was approximately double the LEL (~4 percent by volume), the samples were diluted approximately 2:1 with ambient air to provide a sample that the LEL units could measure. The operating configuration of the GC permitted detection of less than 1 ppm benzene in the diluted stack gas and detected no benzene in the outlet samples. To confirm that the analytical system was capable of the requisite detection, the outlet samples were diluted with benzene calibration gases instead of ambient air and this spiked sample was analyzed. Further, inlet samples at several different dilution ratios were analyzed with the GC and found to contain benzene. Detection of benzene at 0.7 ppm was effected.

LEL Analyzers --

When compared to each other, the LEL analyzers measured total hydrocarbons reasonably well. The response characteristics of the LEL analyzers to various hydrocarbon species are not known, but the field tests showed a fairly consistent relationship, as seen in the time plots (Figure 10) of the individual readings from all the instruments. These plots show that the instruments all followed the same general trend, that is, an increase in one meant an increase in the others. When least-squares linear regressions were calculated between each of the LEL analyzers and the GC, using the LEL response as the dependent variable and the GC response as the independent variable, the correlations were not particularly good (r^2 = 0.4 to 0.8). Comparing the individual LEL analyzers with the average value of all four yielded much better correlations, as shown in Table 6 below. The low value for the Horiba is not surprising, considering its operating difficulties. The high correlations for the catalytic oxidation units are not unexpected considering the detection method.

Benzene/Total Hydrocarbons --

Virtually no benzene (<1 ppm) was found in the exhaust gas samples, but significant amounts were present in the inlet to the condenser. Several tests of the inlet gas to the refrigeration system showed from 0.64 to 5.86 percent of the GC total chromatographable organics were benzene. To analyze the inlet gas with the LEL units, the inlet stream was diluted with ambient air until the LEL readings were on scale. No attempt was made to quantify the actual dilution rate; it was estimated to be about 20:1 at the lowest ratio and about 100:1 at the highest ratio. The sampled gas concentration of benzene for the inlet samples (diluted) ranged from 0.2 ppm to 13.1 ppm, and the undiluted concentration in the inlet gas was estimated to be from 12 to 590 ppm.

No relationship between benzene and total hydrocarbons as measured by the LEL analyzers was observed; however, the same general GC-LEL relationship discussed above held with the inlet samples as with the outlet samples.

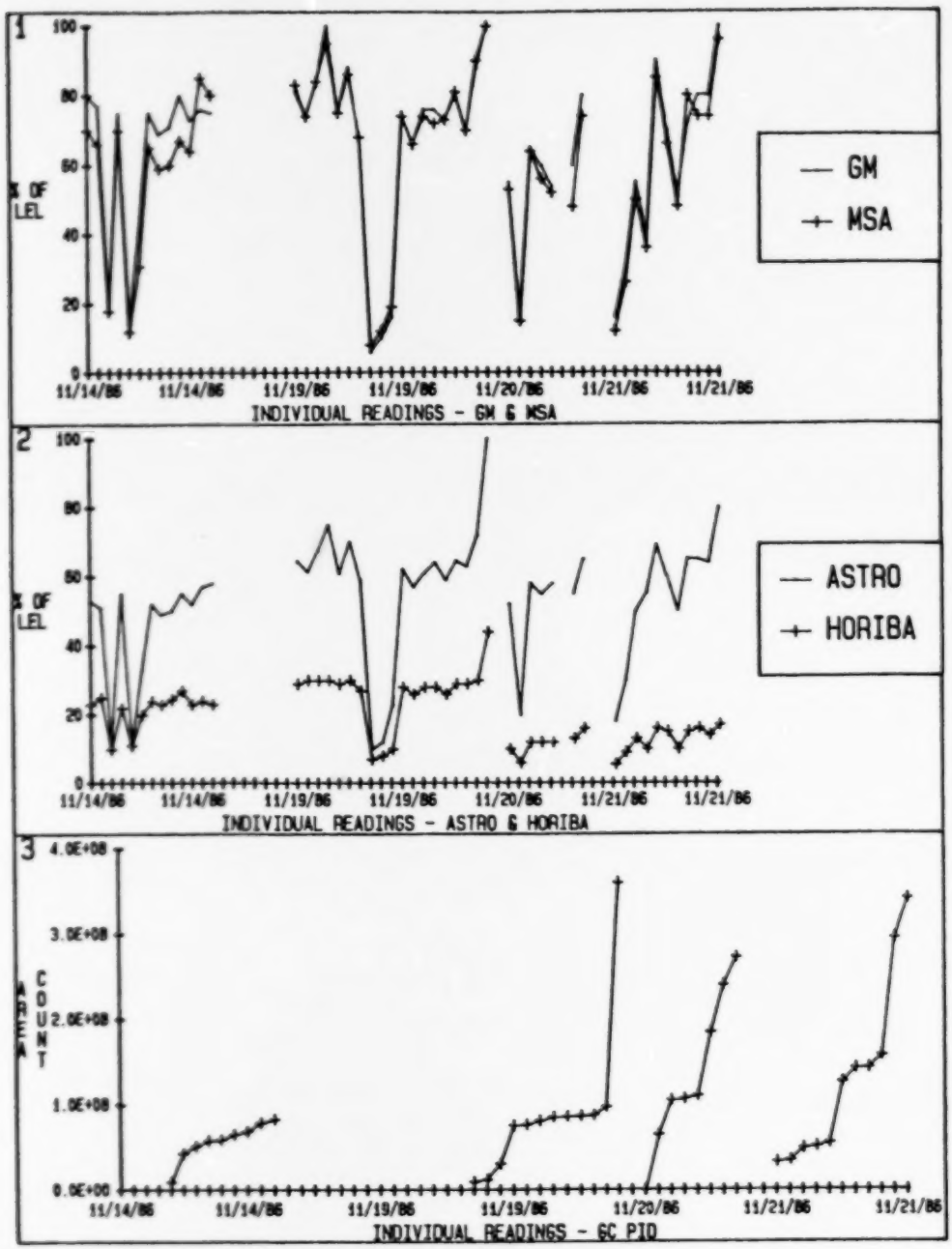


Figure 10. Benzene Monitor Field Test Data

TABLE 6. LEL ANALYZER REGRESSION SUMMARIES

Analyzer	Slope (Standard error)	Intercept	Correlation coefficient
General Monitors	1.323 (0.0298)	-1.545	0.976
MSA	1.321 (0.0257)	-4.354	0.982
Astro	0.980 (0.0390)	4.625	0.929
Horiba	0.377 (0.0411)	1.273	0.636

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APPENDIX A
LEL ANALYZER SUPPLIERS

Name	Address
Astro Resources Corp.	801 Link Road League City, TX 77573 (713) 332-2484
Delphian Corporation	Not available
Foxboro Analytical	Wilks Infrared Center P.O. Box 440 S. Norwalk, CT 06856 (203) 853-1616
General Monitors, Inc.	3019 Enterprise Street Costa Mesa, CA 92626 (714) 540-4895
HNU Systems, Inc.	160 Charlemont Street Newton Highlands, MA 02161 (617) 964-6690
Horiba Instruments, Inc.	1021 Duryea Avenue Irvine, CA 92714 (714) 250-4811
Mine Safety Appliances Co. (MSA)	36 Great Valley Parkway Malvern, PA 19355 (215) 647-7700 (800) MSA-2222
Photovac International Inc.	739B Park Avenue Huntington Long Island, NY 11743 (516) 351-5809
Sentex Sensing Technology	553 Broad Avenue Ridgefield, NJ 07657 (201) 945-3694

APPENDIX B

LABORATORY DATA

REPORT DATE: 03/24/87
HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	UNITS	RELATIVE MASS	RESPONSE
		HNU	TEST	COLUMN		110 oC	RT= .55 MIN				
30-Jun	1A	FID	10	1	NA	90.17	50	OFF	% CHART	4509	ERR
30-Jun	1A	FID	10	1	NA	90.17	50	50	% CHART	4509	0.0111
30-Jun	1A	FID	10	1	NA	50.99	100	55	% CHART	5099	0.0108
30-Jun	1A	FID	10	1	NA	50.99	100	54	% CHART	5099	0.0106
30-Jun	1A	FID	10	1	NA	9.165	100	14	% CHART	917	0.0153
30-Jun	1A	FID	10	1	NA	9.165	100	12.5	% CHART	917	0.0136
30-Jun	1A	FID	10	1	NA	5.289	100	8.5	% CHART	529	0.0161
30-Jun	1A	FID	10	1	NA	5.289	100	6	% CHART	529	0.0113
30-Jun	1A	FID	10	1	NA	1.114	100	3.5	% CHART	111	0.0314
30-Jun	1A	FID	10	1	NA	1.114	100	1.5	% CHART	111	0.0135
30-Jun	1B	PID	100	1	4096	90.17	50	6699368	AC	4509	1486
30-Jun	1B	PID	100	1	4096	90.17	50	6869887	AC	4509	1524
30-Jun	1B	PID	100	1	4096	50.99	100	8254667	AC	5099	1619
30-Jun	1B	PID	100	1	4096	50.99	100	8313376	AC	5099	1630
30-Jun	1B	PID	100	1	4096	9.165	100	2747541	AC	917	2998
30-Jun	1B	PID	100	1	4096	9.165	100	2217791	AC	917	2420
30-Jun	1B	PID	100	1	4096	5.289	100	1615823	AC	529	3055
30-Jun	1B	PID	100	1	4096	5.289	100	1165816	AC	529	2204
30-Jun	1B	PID	100	1	4096	1.114	100	802294	AC	111	7202
30-Jun	1B	PID	100	1	4096	1.114	100	582589	AC	111	5230
01-Jul	2A	FID	1	4	4	50.99	50	22786	AC	2550	8.937
01-Jul	2A	FID	1	4	4	50.99	50	23943	AC	2550	9.391
01-Jul	2A	FID	1	4	4	90.17	25	22132	AC	2254	9.818
01-Jul	2A	FID	1	4	4	90.17	25	25358	AC	2254	11.249
01-Jul	2A	FID	1	4	4	9.165	100	7895	AC	917	8.614
01-Jul	2A	FID	1	4	4	9.165	100	7376	AC	917	8.048
01-Jul	2A	FID	1	4	4	5.289	100	3994	AC	529	7.552
01-Jul	2A	FID	1	4	4	5.289	100	3743	AC	529	7.077
01-Jul	2A	FID	1	4	4	1.114	100	956	AC	111	8.582
01-Jul	2A	FID	1	4	4	1.114	100	1008	AC	111	9.048
01-Jul	2B	PID	1	16	NA	50.99	50	OFF	% CHART	2550	ERR
01-Jul	2B	PID	1	32	NA	50.99	50	90	% CHART	2550	0.0353
01-Jul	2B	PID	1	32	NA	90.17	25	86	% CHART	2254	0.0382
01-Jul	2B	PID	1	32	NA	90.17	25	94	% CHART	2254	0.0417
01-Jul	2B	PID	1	32	NA	9.165	100	31	% CHART	917	0.0338
01-Jul	2B	PID	1	32	NA	9.165	100	28	% CHART	917	0.0306
01-Jul	2B	PID	1	32	NA	5.289	100	16	% CHART	529	0.0303
01-Jul	2B	PID	1	32	NA	5.289	100	14	% CHART	529	0.0265
01-Jul	2B	PID	1	32	NA	1.114	100	4	% CHART	111	0.0359
01-Jul	2B	PID	1	32	NA	1.114	100	4	% CHART	111	0.0359

HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	ATTENUATION D/OUT	ATTENUATION INTEG	CONC PPM	VOL ul	RESPONSE VALUE	RESPONSE UNITS	RELATIVE MASS	RELATIVE RESPONSE
		35% BC-150	ON 100/120	CHROMOSORB P-AW							
			117 oC	CARRIER 30-35 mL/min							
10-Jul	3	PID	1	4	8	50.99	100	443472	AC	5099	86.97
10-Jul	3	PID	1	4	8	50.99	100	441594	AC	5099	86.60
10-Jul	3	PID	1	4	8	90.17	100	736909	AC	9017	81.72
10-Jul	3	PID	1	4	8	90.17	50	422488	AC	4509	93.71
10-Jul	3	PID	1	4	8	90.17	50	377454	AC	4509	83.72
10-Jul	3	PID	1	4	8	9.165	100	81787	AC	917	89.24
10-Jul	3	PID	1	4	8	9.165	100	76165	AC	917	83.10
10-Jul	3	PID	1	4	8	5.289	100	41596	AC	529	78.65
10-Jul	3	PID	1	4	8	5.289	100	34281	AC	529	64.82
10-Jul	3	PID	1	4	8	1.114	100	10334	AC	111	92.76
10-Jul	3	PID	1	4	8	1.114	100	13309	AC	111	119.47
30-Jul	4A	PID	1	4	1	90.17	50	*132411	AC	4509	
30-Jul	4A	PID	1	4	1	90.17	50	305395	AC	4509	67.74
30-Jul	4A	PID	1	4	1	90.17	50	298874	AC	4509	66.29
30-Jul	4A	PID	1	4	1	50.99	50	172992	AC	2550	67.85
30-Jul	4A	PID	1	4	1	50.99	50	175858	AC	2550	68.98
30-Jul	4A	PID	1	4	1	50.99	50	175194	AC	2550	68.72
30-Jul	4A	PID	1	4	1	9.165	100	67671	AC	917	73.84
30-Jul	4A	PID	1	4	1	9.165	100	65471	AC	917	71.44
30-Jul	4A	PID	1	4	1	9.165	100	63626	AC	917	69.42
30-Jul	4A	PID	1	4	1	0	100	0	AC	0	
30-Jul	4A	PID	1	4	1	5.289	100	36367	AC	529	68.76
30-Jul	4A	PID	1	4	1	5.289	100	36797	AC	529	69.57
30-Jul	4A	PID	1	4	1	1.114	100	9125	AC	111	81.91
30-Jul	4A	PID	1	4	1	1.114	100	11176	AC	111	100.32
30-Jul	4B	FID	1	1	NA	90.17	50	*29	% CHART	4509	
30-Jul	4B	FID	1	1	NA	90.17	50	66	% CHART	4509	0.0146
30-Jul	4B	FID	1	1	NA	90.17	50	65	% CHART	4509	0.0144
30-Jul	4B	FID	1	1	NA	50.99	50	35	% CHART	2550	0.0137
30-Jul	4B	FID	1	1	NA	50.99	50	40	% CHART	2550	0.0157
30-Jul	4B	FID	1	1	NA	50.99	50	38	% CHART	2550	0.0149
30-Jul	4B	FID	1	1	NA	9.165	100	14	% CHART	917	0.0153
30-Jul	4B	FID	1	1	NA	9.165	100	14	% CHART	917	0.0153
30-Jul	4B	FID	1	1	NA	9.165	100	14	% CHART	917	0.0153
30-Jul	4B	FID	1	1	NA	0	100	0	% CHART	0	ERR
30-Jul	4B	FID	1	1	NA	5.289	100	8	% CHART	529	0.0151
30-Jul	4B	FID	1	1	NA	5.289	100	7.5	% CHART	529	0.0142
30-Jul	4B	FID	1	1	NA	1.114	100	2	% CHART	111	0.0180
30-Jul	4B	FID	1	1	NA	1.114	100	2	% CHART	111	0.0180

HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	UNITS	RELATIVE MASS	RELATIVE RESPONSE
		35% BC-150 ON 100/120 CHROMOSORB P-AW									
		117 oC CARRIER 30-35 mL/min									
30-Jul	5	PID	1	4	16	90.17	50	311186	AC	4509	69.02
30-Jul	5	PID	1	4	8	90.17	50	321592	AC	4509	71.33
30-Jul	5	PID	1	4	8	90.17	50	309566	AC	4509	68.66
30-Jul	5	PID	1	4	8	50.99	100	336679	AC	5099	66.03
30-Jul	5	PID	1	4	8	50.99	100	353604	AC	5099	69.35
30-Jul	5	PID	1	4	8	9.165	100	77474	AC	917	84.53
30-Jul	5	PID	1	4	8	9.165	X	20852	AC	ERR	ERR
30-Jul	5	PID	1	4	8	9.165	X	18587	AC	ERR	ERR
30-Jul	5	PID	1	4	8	9.165	X	15268	AC	ERR	ERR
30-Jul	5	PID	1	4	8	9.165	100	69932	AC	917	76.30
30-Jul	5	PID	1	4	8	9.165	100	72593	AC	917	79.21
30-Jul	5	PID	1	4	8	5.289	100	41161	AC	529	77.82
30-Jul	5	PID	1	4	8	5.289	100	36691	AC	529	69.37
30-Jul	5	PID	1	4	8	1.114	100	9709	AC	111	87.15
30-Jul	5	PID	1	4	8	1.114	100	8794	AC	111	78.94
31-Jul	6	FID	1	1	8	90.17	100	611672	AC	9017	67.84
31-Jul	6	FID	1	1	8	90.17	50	342209	AC	4509	75.90
31-Jul	6	FID	1	1	8	90.17	50	368250	AC	4509	81.68
31-Jul	6	FID	1	1	8	50.99	100	352989	AC	5099	69.23
31-Jul	6	FID	1	1	8	50.99	100	360890	AC	5099	70.78
31-Jul	6	FID	1	1	8	9.165	100	66322	AC	917	72.36
31-Jul	6	FID	1	1	8	9.165	100	56211	AC	917	61.33
31-Jul	6	FID	1	1	8	5.289	100	33090	AC	529	62.56
31-Jul	6	FID	1	1	8	5.289	100	34322	AC	529	64.89
31-Jul	6	FID	1	1	8	1.114	100	0	AC	111	0.00
31-Jul	6	FID	1	1	8	1.114	100	7501	AC	111	67.33
31-Jul	6	FID	1	1	8	1.114	100	8319	AC	111	74.68
31-Jul	7	FID	1	1	1	1.114	100	8171	AC	111	73.35
31-Jul	7	FID	1	1	1	1.114	100	13428	AC	111	120.54
31-Jul	7	FID	1	1	1	5.289	100	27997	AC	529	52.93
31-Jul	7	FID	1	1	1	5.289	100	29850	AC	529	56.44
31-Jul	7	FID	1	1	1	9.165	50	34649	AC	458	75.61
31-Jul	7	FID	1	1	1	9.165	50	31630	AC	458	69.02
31-Jul	7	FID	1	1	1	50.99	50	182199	AC	2550	71.46
31-Jul	7	FID	1	1	1	50.99	50	188405	AC	2550	73.90
31-Jul	7	FID	1	1	1	90.17	10	59366	AC	902	65.84
31-Jul	7	FID	1	1	1	90.17	10	89267	AC	902	99.00

REPORT DATE: 03/24/87

HNU GC RAW DATA

35% BC-150 ON 100/120 CHROMOSORB P-AW
117 oC CARRIER 30-35 mL/min

DATE	RUN ID	DETECT	ATTENUATION D/IN	D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	UNITS	RELATIVE MASS	RELATIVE RESPONSE
01-Aug	8	FID	1	1	1	0	100	0	AC	0	ERR
01-Aug	8	FID	1	1	1	0	100	0	AC	0	ERR
01-Aug	8	FID	1	1	1	90.17	10	27377	AC	902	30.36
01-Aug	8	FID	1	1	1	90.17	10	26979	AC	902	29.92
01-Aug	8	FID	1	1	1	90.17	10	9642	AC	902	10.69
01-Aug	8	FID	1	1	1	50.99	50	140288	AC	2550	55.03
01-Aug	8	FID	1	1	1	50.99	50	103244	AC	2550	40.50
01-Aug	8	FID	1	1	1	50.99	50	142576	AC	2550	55.92
01-Aug	8	FID	1	1	1	9.165	50	36035	AC	458	78.64
01-Aug	8	FID	1	1	1	9.165	50	43479	AC	458	94.88
01-Aug	8	FID	1	1	1	9.165	50	28355	AC	458	61.88
01-Aug	8	FID	1	1	1	9.165	50	23096	AC	458	50.40
01-Aug	8	FID	1	1	1	5.289	50	17058	AC	264	64.50
01-Aug	8	FID	1	1	1	5.289	50	16001	AC	264	60.51
01-Aug	8	FID	1	1	1	5.289	50	17630	AC	264	66.67
01-Aug	8	FID	1	1	1	1.114	50	0	AC	56	0.00
01-Aug	8	FID	1	1	1	1.114	50	0	AC	56	0.00
06-Aug	11	FID	1	1	1	90.17	50	385945	AC	4509	85.60
06-Aug	11	FID	1	1	1	90.17	50	197078	AC	4509	43.71
06-Aug	11	FID	1	1	1	90.17	50	221130	AC	4509	49.05
06-Aug	11	FID	1	1	1	90.17	50	210831	AC	4509	46.76
06-Aug	11	FID	1	1	1	9.165	100	145869	AC	917	159.16
06-Aug	11	FID	1	1	1	9.165	100	82264	AC	917	89.76
06-Aug	11	FID	1	1	1	9.165	100	77802	AC	917	84.89
06-Aug	11	FID	1	1	1	1.114	100	13929	AC	111	125.04
06-Aug	11	FID	1	1	1	1.114	100	8977	AC	111	80.58
06-Aug	11	FID	1	1	1	1.114	100	2510	AC	111	22.53
06-Aug	11	FID	1	1	1	1.114	100	4730	AC	111	42.46
06-Aug	11	FID	1	1	1	1.114	100	5675	AC	111	50.94
06-Aug	11	FID	1	1	1	9.165	100	70584	AC	917	77.01

REPORT DATE: 03/24/87
HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	D/OUT	INTEG	CONC PPM	VOL µl	RESPONSE VALUE	UNITS	RELATIVE MASS	RELATIVE RESPONSE
	RUN 13		POSSIBLE			DETECTOR		PROBLEMS			
	PID LAMP		CHGD			FID RUNS		FOR VERIF			
07-Aug	13	PID	1	4	8	50.99	100	215506	AC	5099	42.26
07-Aug	13	PID	1	4	8	50.99	100	221063	AC	5099	43.35
07-Aug	13	PID	1	4	8	50.99	100	192692	AC	5099	37.79
07-Aug	13	PID	1	4	8	50.99	100	249842	AC	5099	49.00
07-Aug	13	PID	1	4	PL-8	90.17	100	372763	AC	9017	41.34
07-Aug	13	PID	1	4	PL-8	90.17	100	345730	AC	9017	38.34
07-Aug	13	PID	1	4	PL-8	90.17	100	457506	AC	9017	50.74
07-Aug	13	PID	1	4	HAM-8	90.17	100	363589	AC	9017	40.32
07-Aug	13	PID	1	4	HAM-8	90.17	100	450731	AC	9017	49.99
07-Aug	13	PID	1	4	HAM-8	90.17	100	461087	AC	9017	51.14
07-Aug	13	PID	1	4	8	9.165*	100	124598	AC	ERR	ERR
07-Aug	13	PID	1	4	8	9.165	100	32605	AC	917	35.58
						*CONTAM					
07-Aug	13	FID	1	4	8	90.17	100	383212	AC	9017	42.50
07-Aug	13	FID	1	4	8	90.17	100	345988	AC	9017	38.37
07-Aug	13	FID	1	4	8	90.17	100	313452	AC	9017	34.76
08-Aug	15	FID	1	1	8	90.17	100	280727	AC	9017	31.13
08-Aug	15	FID	1	1	8	90.17	100	324519	AC	9017	35.99
08-Aug	15	FID	1	1	8	90.17	100	288436	AC	9017	31.99
08-Aug	15	FID	1	1	8	90.17	50	126842	AC	4509	28.13
08-Aug	15	FID	1	1	8	90.17	50	164509	AC	4509	36.49
08-Aug	15	FID	1	1	8	90.17	50	228691	AC	4509	50.72
08-Aug	16	PID	1	1	16	90.17	100	553669	AC	9017	61.40
08-Aug	16	PID	1	1	8	90.17	100	1283895	AC	9017	142.39
08-Aug	16	PID	1	1	16	90.17	100	1336503	AC	9017	148.22
08-Aug	16	PID	1	4	8	90.17	100	89132	AC	9017	39.54
11-Aug	17	PID	1	4	8	50.99	100	56528	AC	5099	44.34
11-Aug	17	PID	1	4	8	50.99	100	59568	AC	5099	46.73
11-Aug	17	PID	1	4	2	50.99	100	94387	AC	5099	74.04
11-Aug	17	PID	1	4	2	50.99	100	94944	AC	5099	74.48
11-Aug	17	FID	1	4	2	50.99	100	48000	AC	5099	37.65
11-Aug	17	FID	1	4	2	50.99	100	50668	AC	5099	39.75
11-Aug	17	FID	1	1	2	50.99	100	205243	AC	5099	40.25
11-Aug	17	FID	1	1	2	50.99	100	215823	AC	5099	42.33
11-Aug	17	FID	1	4	8	50.99	100	183460	AC	5099	35.98
11-Aug	17	FID	1	4	8	50.99	100	230205	AC	5099	45.15

REPORT DATE: 03/24/87

HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	ATTENUATION D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	RESPONSE UNITS	RELATIVE MASS	RELATIVE RESPONSE
	35% BC-150 ON 100/120 CHROMOSORB P-AW 117 oC CARRIER 30-35 mL/min										
12-Aug	18	PID	10	1	4	90.17	100	86280	AC	9017	95.69
12-Aug	18	PID	10	1	4	90.17	100	90844	AC	9017	100.75
12-Aug	18	PID	10	1	4	90.17	50	52733	AC	4509	116.96
12-Aug	18	PID	10	1	4	90.17	50	58804	AC	4509	130.43
12-Aug	18	PID	10	1	AZ-PT-4	90.17	100	73508	AC	9017	81.52
12-Aug	18	PID	10	1	4	90.17	100	80996	AC	9017	89.83
12-Aug	18	PID	10	1	4	90.17	50	48838	AC	4509	108.32
12-Aug	18	PID	10	1	4	90.17	50	41772	AC	4509	92.65
12-Aug	18	PID	10	1	4	90.17	20	17205	AC	1803	95.40
12-Aug	18	PID	10	1	4	90.17	20	24883	AC	1803	137.98
12-Aug	18	PID	10	1	4	90.17	20	25627	AC	1803	142.10
12-Aug	18	PID	10	1	4	50.99	100	62901	AC	5099	123.36
12-Aug	18	PID	10	1	4	50.99	100	48083	AC	5099	94.30
12-Aug	18	PID	10	1	4	50.99	100	50472	AC	5099	98.98
12-Aug	18	PID	10	1	4	50.99	100	49219	AC	5099	96.53
12-Aug	18-G	PID	10	1	4	GV-2%	50	61540	NOT PURGED		
12-Aug	18-G	PID	10	1	4	GV-2%	50	80424			
12-Aug	18-G	PID	10	1	4	GV-2%	50	77438			
12-Aug	18-G	PID	10	1	4	GV-2%	50	83716			
12-Aug	19	FID	1	2	16	GV-2.00%	50	293120	AC		
12-Aug	19	FID	1	2	16	GV-2.00%	50	275617	AC		
12-Aug	19	FID	1	2	16	GV-2.00%	50	202950	AC		
12-Aug	19	FID	1	2	16	90.17	100	204216*	AC	9017	ERR
12-Aug	19	FID	1	2	16	90.17	100	237931*	AC	9017	ERR
12-Aug	19	FID	1	2	16	90.17	100	223431	AC	9017	24.78
12-Aug	19	FID	1	2	16	90.17	100	261162	AC	9017	28.96
12-Aug	19	FID	1	2	16	90.17	100	213188	AC	9017	23.64
12-Aug	19	FID	1	2	8	90.17	100	262801	AC	9017	29.15
12-Aug	19	FID	1	2	8	90.17	100	214513	AC	9017	23.79
12-Aug	19	FID	1	2	8	90.17	100	301206	AC	9017	33.40
12-Aug	19	FID	1	2	8	90.17	100	194404	AC	9017	21.56
12-Aug	19	FID	1	2	16	90.17	50	155085	AC	4509	34.40
12-Aug	19	FID	1	2	16	90.17	50	154978	AC	4509	34.37
12-Aug	19	FID	1	2	16	90.17	20	NG	AC	1803	ERR
12-Aug	19	FID	1	2	16	90.17	20	NG	AC	1803	ERR

*RESID CONTAM.

REPORT DATE: 03/24/87

HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	ATTENUATION D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	RESPONSE UNITS	RELATIVE MASS	RELATIVE RESPONSE
		35% BC-150	ON 100/120	CHROMOSORB P-AW							
		117 oC		CARRIER 30-35 mL/min							
15-Aug	20	FID	1	1	4	1.114	100	19284	AC	111	173.11
15-Aug	20	FID	1	1	4	1.114	100	9763	AC	111	87.64
15-Aug	20	FID	1	1	4	90.17	100	296022	AC	9017	32.83
15-Aug	20	FID	1	1	4	90.17	100	329858	AC	9017	36.58
15-Aug	20	FID	1	1	4	90.17	100	411322	AC	9017	45.62
15-Aug	20	FID	1	1	4	90.17	100	371196	AC	9017	41.17
15-Aug	20	FID	1	1	4	90.17	100	316868	AC	9017	35.14
						===	100	345053	====	AVG	38.2669
15-Aug	20	FID	1	1	4	GV-1.99%	20	232637	AC		
15-Aug	20	FID	1	1	4	GV-1.99%	20	292542	AC		
15-Aug	20	FID	1	1	4	GV-1.99%	20	261538	AC		
15-Aug	20	FID	1	1	4	GV-1.99%	20	320824	AC		
						===	20	276885	====		
16-Aug	21	FID	1	1	HAM-8	90.17	100	757843	AC	9017	84.05
16-Aug	21	FID	1	1	HAM-8	90.17	100	822060	AC	9017	91.17
16-Aug	21	FID	1	1	HAM-8	90.17	100	830541	AC	9017	92.11
16-Aug	21	FID	1	1	HAM-8	90.17	50	399821	AC	4509	88.68
16-Aug	21	FID	1	1	HAM-8	50.99	100	469897	AC	5099	92.15
16-Aug	21	FID	1	1	HAM-8	50.99	100	486342	AC	5099	95.38
16-Aug	21	FID	1	1	HAM-8	50.99	100	559928	AC	5099	109.81
16-Aug	21	FID	1	1	HAM-8	9.165	100	90512	AC	917	98.76
16-Aug	21	FID	1	1	HAM-8	9.165	100	84429	AC	917	92.12
16-Aug	21	FID	1	1	HAM-8	5.289	100	44530	AC	529	84.19
16-Aug	21	FID	1	1	HAM-8	5.289	100	44756	AC	529	84.62
16-Aug	21	FID	1	1	HAM-8	1.11	100	0	AC	111	0.00
16-Aug	21	FID	1	1	HAM-8	1.11	100	0	AC	111	0.00
20-Aug	22	PID	1	4	PS-8	90.17	100	451992	AC	9017	50.13
20-Aug	22	PID	1	4	PS-8	90.17	100	583747	AC	9017	64.74
20-Aug	22	PID	1	4	PS-8	90.17	100	449506	AC	9017	49.85
20-Aug	22	PID	1	4	PS-8	90.17	100	777337	AC	9017	86.21
20-Aug	22	PID	1	4	PS-8	90.17	100	741602	AC	9017	82.24
		AZ-PID									
20-Aug	22	PID	1	4	PS-16	90.17	100	923150	AC	9017	102.38

HNU GC RAW DATA

DATE	RUN ID	DETECT	ATTENUATION D/IN	ATTENUATION D/OUT	INTEG	CONC PPM	VOL ul	RESPONSE VALUE	RESPONSE UNITS	RELATIVE MASS	RELATIVE RESPONSE
		35% BC-150	ON 100/120	CHROMOSORB P-AW							
			117 oC	CARRIER 30-35 mL/min							
21-Aug	23	PID	1	4	PS-16	90.17	100	596529	AC	9017	66.16
21-Aug	23	PID	1	4	PS-16	90.17	100	411431	AC	9017	45.63
21-Aug	23	PID	1	4	PS-16	90.17	100	467444	AC	9017	51.84
21-Aug	23	PID	1	4	PS-16	90.17	100	153202	AC	9017	16.99
21-Aug	23	PID	1	4	PS-16	90.17	100	544916	AC	9017	60.43
21-Aug	23	PID	1	4	PS-16	90.17	50	337235	AC	4509	74.80
21-Aug	23	PID	1	4	PS-8	90.17	50	255740	AC	4509	56.72
21-Aug	23	PID	1	4	PS-8	90.17	50	97947	AC	4509	21.72
21-Aug	23	PID	1	4	PS-8	90.17	100	467214	AC	9017	51.81
21-Aug	24	FID	1	1	PS-8	90.17	100	323345	AC	9017	35.86
21-Aug	24	FID	1	1	PS-8	90.17	100	303780	AC	9017	33.69
21-Aug	24	FID	1	1	PS-8	90.17	100	503473	AC	9017	55.84
21-Aug	24	FID	1	1	PS-8	90.17	100	296664	AC	9017	32.90
21-Aug	24	FID	1	1	HAM-8	90.17	100	757843	AC	9017	84.05
21-Aug	24	FID	1	1	HAM-8	90.17	100	822060	AC	9017	91.17
21-Aug	24	FID	1	1	HAM-8	90.17	100	830541	AC	9017	92.11
21-Aug	24	FID	1	1	HAM-8	90.17	50	399821	AC	4509	88.68
21-Aug	24	FID	1	1	HAM-8	50.99	100	469897	AC	5099	92.15
21-Aug	24	FID	1	1	HAM-8	50.99	100	486342	AC	5099	95.38
21-Aug	24	FID	1	1	HAM-8	50.99	100	559928	AC	5099	109.81
21-Aug	24	FID	1	1	HAM-8	0	100	47258	AC	0	ERR
21-Aug	24	FID	1	1	HAM-8	0	100	0	AC	0	ERR
21-Aug	24	FID	1	1	HAM-8	9.165	100	84429	AC	917	92.12
21-Aug	24	FID	1	1	HAM-8	9.165	100	90512	AC	917	98.76
21-Aug	24	FID	1	1	HAM-8	5.289	100	44530	AC	529	84.19
21-Aug	24	FID	1	1	HAM-8	5.289	100	44756	AC	529	84.62
21-Aug	24	FID	1	1	HAM-8	1.114	100	0	AC	111	0.00
21-Aug	24	FID	1	1	HAM-8	1.114	100	0	AC	111	0.00

PHOTOVAC RAW DATA REPORT DATE: 03/24/87

DATE	CAL	VOL	INJ	GAIN		ANALYTE	ANALYSIS #1	#2	#3	AVG	RSD
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.7			12.70	NA
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.6			12.60	NA
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.5			12.50	NA
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.4			12.40	NA
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.3			12.30	NA
26-Aug	NONE	300	A	0.3 10	VS	50.99	12.2			12.20	NA
26-Aug	50.99	300	A	0.3 10	PPM	9.165	18.48	15.51		17.00	12.36
26-Aug	50.99	300	A	0.3 10	PPM	9.165	14.63	13.55	12.7	13.63	7.10
26-Aug	50.99	300	A	0.3 10	PPM	9.165	13.32	12.55	12.21	12.69	4.48
26-Aug	50.99	300	A	0.3 10	PPM	50.99	48.78	45.53	45.04	46.45	4.38
26-Aug	50.99	300	A	0.3 10	PPM	50.99	44.94	43.9	44.25	44.36	1.19
26-Aug	50.99	300	A	0.3 10	PPM	1.114	5.324	4.455	3.699	4.49	18.10
26-Aug	50.99	300	A	0.3 10	PPM	1.114	3.784	2.994	2.59	3.12	19.45
26-Aug	50.99	300	A	0.3 10	PPM	1.114	3.229	2.471	2.124	2.61	21.67
26-Aug	50.99	300	A	0.3 10	PPM	90.17	79.76	80.8	81.5	80.69	1.09
26-Aug	50.99	300	A	0.3 10	PPM	90.17	75.02	74.55	74.31	74.63	0.48
26-Aug	50.99	300	A	0.3 10	PPM	50.99	56.34	57.85	54.59	56.26	2.90
26-Aug	50.99	300	A	0.3 10	PPM	50.99	50.05	49.82		49.94	0.28

BULK TERMINAL FIELD DATA- GC/LEL ANALYSES

SAMPLE DATE	TIME	LEL ANALYZERS % OF LEL GM	MSA	AST	HOR	RUN	PID	GC/PID AREA COUNT BENZENE	REPORT	ABSOLUTE
11/14/86	11:13	75	70	55	22	NA				
11/14/86	11:15	75	80	58	23	4	10	0	8,355,689	8.36E+07
11/14/86	11:18	76	85	57	24	5	10	0	7,918,792	7.92E+07
11/14/86	11:24	80	70	53	23	NA				
11/14/86	11:41	73	64	52	23	7	10	0	6,893,891	6.89E+07
11/14/86	11:47	19	18	12	10	NA				
11/14/86	11:54	75	65	52	24	8	100	0	521,440	5.21E+07
11/14/86	12:02	77	66	51	25	NA				
11/14/86	12:06	71	60	50	24.5	9	100	0	596,212	5.96E+07
11/14/86	12:34	69	59	49	23	12	100	0	587,609	5.88E+07
11/14/86	12:45	42	31	33	20	13	100	0	437,752	4.38E+07
11/14/86	12:54	15	12	11	11	14	100	0	100,046	1.00E+07
11/14/86	13:54	80	67	55	27	15	100	0	655,537	6.56E+07
11/19/86	10:45	16	19	23	10	2	10	0	3,116,019	3.12E+07
11/19/86	10:55	10	12	12	8	3	10	NI	1,271,111	1.27E+07
11/19/86	11:00	100	95	75	30	NA				
11/19/86	11:02	88	86	70	30	NA				
11/19/86	11:06	88	90	72	30	4	10	0	9,788,823	9.79E+07
11/19/86	11:19	76	72	64	28	5	10	0	8,595,379	8.60E+07
11/19/86	11:32	6	8	10	7	6	10	0	990,639	9.91E+06
11/19/86	11:55	73	73	59	26	8	10	0	8,662,294	8.66E+07
11/19/86	12:35	70	70	63	29	12	10	0	8,832,173	8.83E+07
11/19/86	12:50	76	74	61	28	13	10	0	8,177,508	8.18E+07
11/19/86	12:54	76	75	61	29	NA				
11/19/86	14:07	74	74	62	28	16	10	0	7,603,144	7.60E+07
11/19/86	14:24	66	66	57	26	17	10	357,967	7,707,239	7.71E+07K
11/19/86	14:26	68	68	59	27	NA				
11/19/86	14:47	80	81	64.	29	18	10	60,123	8,742,642	8.74E+07
11/19/86	14:49	74	74	61.	30	NA				
11/19/86	14:58	83	84	67.	30	NA				
11/19/86	15:01	81	83	64.	29	NA				
11/19/86	15:03	100	100	100	44	19	10	0	36,067,409	3.61E+08K

BULK TERMINAL FIELD DATA- GC/LEL ANALYSES

SAMPLE DATE	TIME	LEL ANALYZERS % OF LEL GM	MSA	AST	HOR	RUN	PID	GC/PID AREA COUNT BENZENE	REPORT	ABSOLUTE
11/20/86	10:23	55	53	52	10	5	10	0	29,364	2.94E+05
11/20/86	10:28	54	52	58	12	6	10	0	11,061,525	1.11E+08
11/20/86	10:37	60	56	55	12	9	10	0	10,715,282	1.07E+08
11/20/86	11:02	65	64	58	12	10	10		10,568,899	1.06E+08
11/20/86	13:06					13	10	144,358	18,467,689	1.85E+08
11/20/86	13:40	60	48	55	13	16	10	153,966	24,002,483	2.40E+08
11/20/86	14:01	15	15	20	6	17	10	47,642	6,519,926	6.52E+07
11/20/86	14:29	80	74	65	16	18	10	225,239	27,283,327	2.73E+08
11/21/86	10:18	52	48	50	10	2	10	494,291	14,232,345	1.42E+08
11/21/86	10:31	80	74	64	14	3	10	173,055	29,520,401	2.95E+08
11/21/86	10:47	100	96	80	17	4	10	140,161	34,135,976	3.41E+08
11/21/86	11:02	16	12	18	5.5	5	10	46,645	3,328,264	3.33E+07
11/21/86	11:17	30	26	30	9	7	10	7,533	3,533,052	3.53E+07
11/21/86	13:01	40	36	55	10	10	10	0	5,161,244	5.16E+07
11/21/86	13:14	90	85	69	16	12	10	0	5,534,892	5.53E+07
11/21/86	13:27	72	80	65	15	13	10	0	14,286,615	1.43E+08
11/21/86	13:43	55	50	50	13	14	10	0	4,964,207	4.96E+07
11/21/86	13:57	80	74	65	16	15	10	0	15,737,095	1.57E+08
11/21/86	14:24	70	66	60	15	16	10	0	12,631,520	1.26E+08

APPENDIX C

EXAMPLE INSTRUMENT OUTPUTS

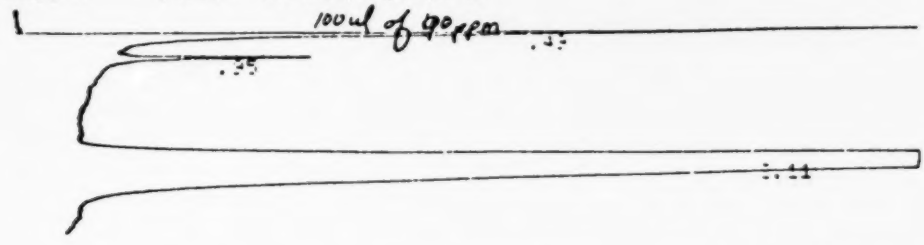
INTEGRATE AREA - B

FID · CONFIGURATION 1 x 1 7/31/86

dump @ 201°C

CHANNEL A INJECT 07/31/86 11:52:01

100 ul of 90 ppm



07/31/86 11:52:01 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 07 INDEX 1 CALIB

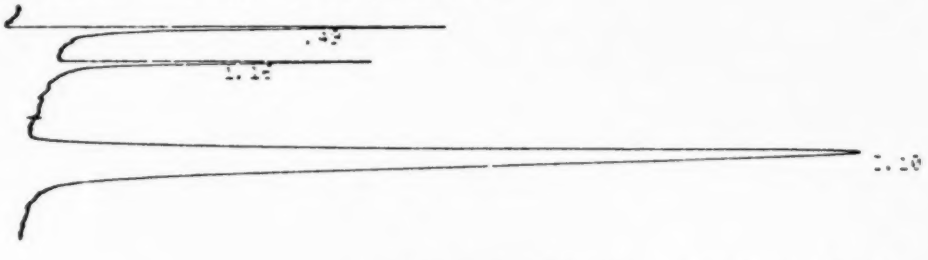
PEAK #	AREA%	RT	AREA BC
1	8.562	0.49	58092 01
2	1.278	0.35	8671 01
1	90.161	1.11	611761 01
TOTAL	100.		678524

RUN 6

KD

50 ul of 90 ppm Benzene

CHANNEL A INJECT 07/31/86 11:57:20

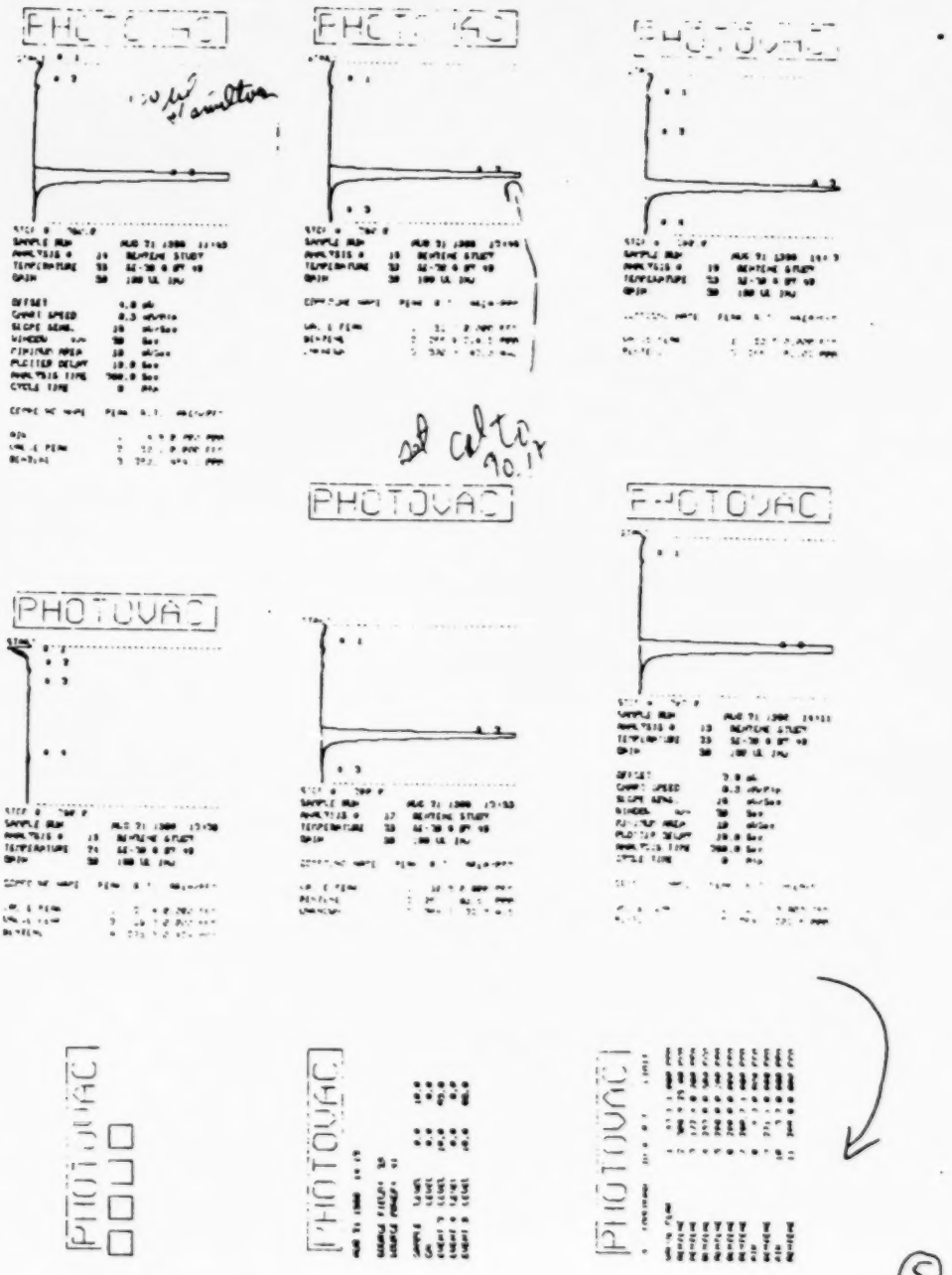


07/31/86 11:57:20 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 08 INDEX 1 CALIB

PEAK #	AREA%	RT	AREA BC
1	7.193	0.49	28618 01
2	4.529	1.16	17997 01
1	88.107	1.1	348209 01
TOTAL	100.		394824

VARIAN INSTRUMENT GROUP 00-997140-01


PHOTOVAC
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PHOTOVAC
PHOTOVAC
PHOTOVAC

SCENTOR
08/05/86
13:52
SAMPLE TIME
005
DELAY TIME
2.0
FILAMENT ON
TIME 4.0
INHIBIT TIME
120
OF PEAKS 1
PEAK NO. 01
BENZENE
PPM 1.11
THRSH 0.00
REPETITION
RATE 6
RECALIBRATE
RATE 2
TEMPERATURE
50
CHART WINDOW
3
TLA HRS 0
ALARM DIS
PRT OPT ALRM
BACKFLSH OPT
OFF
ANALYSIS OPT
NORMAL

CALIBRATION
08/05/86
13:52

#1 BENZENE RT=
222 PPM 1.11

ANALYSIS
08/05/86
13:57

#1 BENZENE RT=
219 PPM 4.04

CALIBRATION
08/05/86
14:07

#1 BENZENE RT=
219 PPM 1.11

ANALYSIS
08/05/86
14:02

9.17 ppm

#1 BENZENE RT=
219 PPM 7.19

ANALYSIS
08/05/86
14:13

#1 BENZENE RT=
216 PPM 3.63

ANALYSIS
08/05/86
14:18

RT=

#1 BENZENE
218 PPM 6.30

(43)